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SOME ASPECTS OF THE ORGANOMETALLIC CHEMISTRY OF PENTAFLUOROPHENYL COMPOUNDS AND OF RHODIUM AND IRIDIUM CYCLOPENTADIENYLS

by

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A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
FALL, 1970

ABSTRACT

A number of pentafluorophenyl compounds have been prepared and by measurement of their ^{19}F nmr spectra, information has been gained concerning π-electronic interactions in these molecules. Methods of forming $C_6F_5Si(CH_3)_2X$ [Where X = H, CH_3, C_6F_5, OCH_3, $N(CH_3)_2$ or $N(H)C_6H_5$] and $R_3MYC_6F_5$ [where R = CH_3 or C_6H_5, M = Si, Ge, Sn or Pb and Y = O, S or NH] are described and some interpretations of the spectroscopic results are proposed.

Derivatives of $C_6F_5Mn(CO)_5$ have been prepared by replacement of one carbonyl group with the ligands $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, $P(OC_6H_5)_3$, C_5H_5N and replacement of two carbonyl groups with $P(n\text{-}C_4H_9)_3$, $P(OC_2H_5)_3$, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and $CH_3SCH_2CH_2SCH_3$. Carbonyl stretching frequencies and ^{19}F nmr parameters are discussed in terms of changes in electron density in the molecules.

Oxidative addition reactions have been carried on on $CpRh(CO)_2$ ($Cp = \pi C_5H_5$) and related compounds. Triphenyl and tribenzylsilanes react with $CpRh(CO)_2$ to yield $CpCORh(H)SiR_3$ whereas only a bis-silyl derivative, $CpCORh(SiCl_3)_2$, is isolated from the reaction with trichlorosilane. Compounds of the type $CpCOXRhMX_3$ (M = Ge, Sn; X = Cl, Br or I) have been formed by treatment of $CpRh(CO)_2$ with the halides of Ge(IV) and Sn(IV) while Sn(II) chloride and bromide afford oligomeric and polymeric species.

Reactions of $CpRhP(CH_3)_2C_6H_5(CO)$, $CpIrP(C_6H_5)_3(CO)$,

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and $CpRhP(C_6H_5)_3(C_2H_4)$ with halogens and alkyl halides have been studied. Halogens gave dihalides with elimination of carbon monoxide or ethylene, often with evidence for an ionic intermediate, e.g. $[CpIrP(C_6H_5)_3(CO)X]^+X^-$. It appears that ionic compounds were similarly formed from alkyl halides (RX). Such derivatives have been isolated for iridium, i.e. $[CpIrP(C_6H_5)_3(CO)R]^+X^-$, but the more stable products for the rhodium compounds mentioned above were $CpRhP(CH_3)_2$-$C_6H_5(COR)X$ and $CpRhP(C_6H_5)_3RX$ respectively.

ACKNOWLEDGMENTS

The author wishes to express sincere appreciation and gratitude to:

Dr. W. A. G. Graham for his guidance, patience and help in the course of this work.

The members of Dr. Graham's research group, particularly Dr. M. G. Hogben, Dr. A. J. Hart-Davis and Mr. R. K. Pomeroy for assistance in many ways.

Mrs. Darlene Mahlow and Mrs. Andrea Dunn for prompt and accurate microanalytical measurements.

Mrs. Mary Waters for her excellent preparation of this manuscript.

The Province of Alberta for a Research Fellowship and the National Research Council of Canada for a Postgraduate Scholarship.

Thanks also to the University of Alberta for other financial assistance.

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CHAPTER I

INTRODUCTION

The Participation of "d" Orbitals in the π-Bonding of Organometallic Compounds

Early in the development of organometallic chemistry it became clear that many observations in this field could be rationalised by π-bonds involving d orbitals. Features such as molecular geometry and the stability and reactivity of these compounds have been explained using this concept.

The Si-Cl bonds in $SiCl_4$ were found to be anomalously short compared to the value derived from sums of covalent radii and in 1934 this was attributed to π-bonding (1). Shortly after, the multiple bond character of the metal-carbonyl linkage in tetracarbonylnickel was indicated by measurement of the Ni-C distances (2). In fact the first proposal of such bonding in tetracarbonylnickel was made by Langmuir (3) in 1921, on the basis of the electroneutrality principle, but at that time there was little support for the new idea. A milestone was reached in the preparation of ferrocene (4,5) in 1951 and π-bonding was invoked to explain the great stability of this interesting compound (6).

Such examples of multiple bonding are usefully classified according to the nature of the π-orbitals which are involved with metal d orbitals, and by the manner in which this involvement takes place (7). It must be recognised

that the d orbitals mentioned in the following discussions are likely to be hybrids having some p and s character. The general value of the resulting ideas is, however, reduced little by this simplification.

Orbitals of d type may accept electrons from a p orbital on an adjacent atom, (p→d)π, or electron density may be removed from a d orbital to a p orbital, (d→p)π. A third type is obviously (d→d)π interaction. These classes are discussed below.

(p→d)π Bonding - As already mentioned the bond shortening in $SiCl_4$ (1) was justified on the basis of a π bond, specifically by donation of 3p electrons from chlorine to the empty 3d orbitals of silicon. Although most chemists now believe this to be acceptable (8), alternative explanations were put forward to avoid the π-bonding proposal.

The classic example of (p→d)π bonding was found in the compound trisilylamine, $(H_3Si)_3N$, which was shown to be planar (9). The planarity was attributed to extensive delocalisation of the nitrogen lone pair into the silicon 3d orbitals. The very weakly basic character of the nitrogen in this molecule had already been noted (10). Similarly $(H_3Si)_3P$ has been found to be planar (11) although analogous germyl systems have a pyramidal skeleton (12). It should be realised, however, that planarity is not an essential requirement for π-bonding (13) with the result that (p→d)π interactions are not necessarily negligible in $(H_3Ge)_3P$.

The $Si\hat{O}Si$ angle in $(H_3Si)_2O$ is consistent with some π bonding and is accepted as 141° (14) although early work indicated that it approached 180°. The corresponding angle in $(H_3Ge)_2O$ is 125.6° and in $(H_3Ge)_2S$ it is 99.1° (15), thus making π-bonding likely in the former and not in the latter compound. Since angles cannot reliably be taken as measures of π-bonding, stronger evidence for this proposal is derived from the bond-shortening observed for the Ge-O and not for Ge-S (15). From studies of trends in basicity, similar π-bonding has been proposed in many compounds containing the bonds Si-O, Si-S and Ge-O (16,17), although not unequivocally in the latter case.

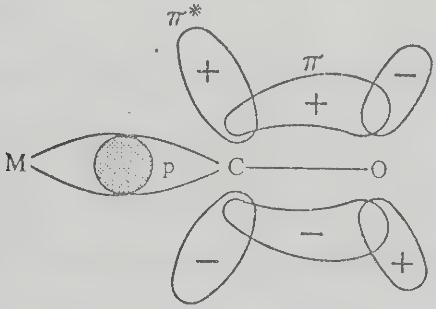
Some removal of π electrons from a directly bonded aromatic system into silicon d orbitals has also been suggested (18) and indeed there is evidence for a similar interaction of silicon with aliphatic carbon (18).

An nmr study using molecules enriched with ^{15}N gave results from which the absence of (Si-N)π-bonding was proposed (19). It was later realised (20) that the results suggested only that the nitrogen was sp^3 hybridised and this does not eliminate the possibility of π-bonding (13). Confusion has also arisen in the π-bonding of halogens to silicon, not in the general acceptance of such bonding but in the order of strength with the different halogens (21,22). It would be very surprising if the strongest π-bond were to iodine (21), since there is no evidence of

of π-bonding from silicon to the heavier members of Group V and Group VI, antimony and tellurium.

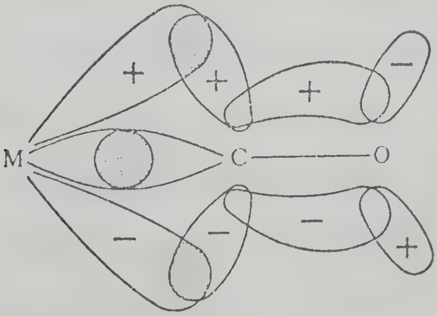
(d→p)π Bonding - Easily available filled or partly filled d orbitals are found in transition metals and thus it becomes possible that (d→p)π bonding would occur in which electron density is lost from the metal to suitable pπ orbitals of a ligand. Such bonding is considered to be present between transition metals and ligands such as CO, NO^+, CN^-, CNR (23) and N_2 (24).

The bonding in the carbonyls is probably the most suitable representative example since these derivatives are the most studied and the best understood (23). The overlap of a filled carbon σ orbital with an empty σ orbital (I)



I

is augmented by the π overlap of a filled d orbital with an empty antibonding p orbital (II)



II

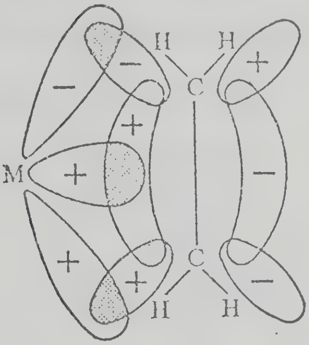
Since the drift of electrons by one mechanism enhances the drift in the opposite direction, by the second mechanism, the bonding process is termed synergic. The result is a very low dipole moment for the M-C bond, suggesting a close approach to electroneutrality. Measurements of bond lengths and vibrational spectra are consistent with the multiple nature of the M-CO bonds. Especially important are the CO stretching frequencies since changes in these frequencies are greatly dependent on the amount of electron density given to the π^* orbitals (25). Such donation reflects the readiness of the other metal ligands to compete for d electrons and thus provides a qualitative method to observe the π-bonding ability of these additional ligands.

Other ligands which bond in similar fashion to carbon monoxide, vary in their σ-donor and π-withdrawal abilities. Thus isocyanides, although isoelectronic with CO, form better σ bonds and weaker π bonds (26) and in the compound $(CO)_5Mo(CNR)$ there is evidence suggesting that almost all back bonding is to the five carbonyls (26).

Multiple bonding in metal perfluoroalkyls has also been proposed and strongest evidence comes from M-C bond shortening (27). This is attributed to $d\pi \rightarrow \sigma^*$ bonding, despite the relatively high energy of σ^* orbitals.

Considerations similar to those in the bonding of carbonyls also apply to the olefin complexes of transition

metals (28). In the case of the olefins their π electrons are themselves involved in the primary σ bond (III). Back



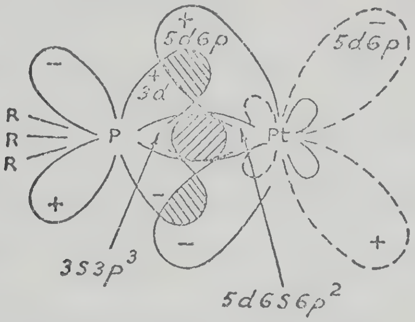
III

bonding then takes place from the metal d to the ligand π* orbital. This is called a μ bond to emphasise the difference between it and the bonding of a carbonyl group, for example.

Similar ideas may be applied to metal complexes of polyenes and acetylenes. The bonding of π-cyclopentadienyl and π-benzene complexes involves related processes but is best described by a molecular orbital treatment (29,30). In such a treatment π orbitals are very important and in ferrocene are considered to be the chief source of bonding (30).

(d→d)π Bonding - Donation through a π system of penultimate metal d electrons to an ultimate d shell of a ligand has frequently been suggested (7); prime examples are trivalent phosphorus or arsenic or divalent sulfur complexes with transition metals. Chatt and coworkers (31, 32,33) have made an extensive study of such bonding in square planar derivatives of platinum. Thus in a trialkyl-

phosphine platinum compound there is a σ bond between the phosphorus $3s3p^3$ and platinum $5d6s6p^2$ orbitals and π withdrawal of electron density from the platinum 5d6p to the empty phosphorus 3d orbitals (IV). Similar, although weaker,



IV

π withdrawal is thought to occur with ligands complexed through Sb(III), Se(II), Te(II), Cl, Br or I.

In square planar complexes, and to a lesser extent in octahedral, some groups have the ability to direct substitution into the position *trans* to themselves and to affect markedly the rate of reaction (34,35). This is the so-called *trans* effect. An explanation of this effect uses the concept of π-bonding to increase the electron affinity of the metal (32) and to stabilise the intermediate (36). Thus observations of such reactions have led to a scaling of the relative π-bonding abilities of groups. An approximate ordering (35) gives, CO, CN^-, $C_2H_4 > PR_3 > SC(NH_2)_2 > NO_2^-, I^-, SCN^- > Br^-, Cl^- > NH_3$, H_2O.

Ordering by π-bonding ability has also been deduced by a study of the change in C-O stretching frequencies in

ligand-substituted metal carbonyls (37). This has led to the following series (38), NO > CO > PF_3 > $SbCl_3$ > $AsCl_3$> PCl_3 > $P(OPh)_3$ > $CH_3C_6H_4NC$ > $P(OMe)_3$ > PPh_3 > SEt_2 > PMe_3. Such ordering does however overlook the undoubted difference in σ bonding properties of ligands (39).

More recent work suggests that one-electron ligands bonded through Si, Ge or Sn are also capable of accepting π-electron density from a transition metal into their empty d orbitals (39). The group $SnCl_3$ has a *trans* effect, and presumably a π-bonding ability, close to CN^- (40). On replacement of chlorine by aryl or alkyl groups the change in π-bonding remains unclear (39,41).

Structural investigations on silyl-transition metal compounds have revealed silicon-metal bond shortening (42,43) which was rationalised by (d→d)π bonding. Such bonding may also be responsible for the observation of conformational effects (44) in the infrared spectra of similar silicon compounds. Silicon is also thought to be able to form (d→d)π bonds to adjacent silicon atoms (45), thus explaining the high stability of $[(CH_3)_3Si]_3Si^-$. In such compounds, however, (p→d)π bonding is likely and difference between the two possibilities cannot be observed.

Transition metals are also capable of π-bonding with themselves (46). The extreme example at the present time is $Re_2Cl_8^{2-}$ (47,48,49) which has an Re-Re bond order of four

one bond of σ symmetry, two of π character (degenerate) and the fourth of δ character.

CHAPTER II

PREPARATION AND PROPERTIES OF SOME PENTAFLUOROPHENYL GROUP IV COMPOUNDS

Recent work at this laboratory (50,51,52,53) has shown a linear relationship between a coupling constant and a chemical shift which may be obtained from the ^{19}F nmr spectra of pentafluorophenyl derivatives. Further it has been found that, for a given compound, an indication of π-electronic interactions with the perfluoroaromatic system may be gained from the appropriate nmr parameters.

Of considerable current interest is the π-bonding of systems containing Group IV elements, particularly the case of the silicon-nitrogen bond as noted in Chapter I. It therefore seemed pertinent to prepare a series of suitable compounds for use in a study involving this new method. In this chapter are reported the methods of preparation and selected properties of the compounds $C_6F_5Si(CH_3)_2X$ (where X = H, CH_3 C_6F_5, OCH_3, $N(CH_3)_2$ or $N(H)C_6H_5$) and the compounds $R_3MYC_6H_5$ (R = CH_3 or C_6H_5, M = Si, Ge, Sn or Pb and Y = O, S or NH). A few of these compounds have been prepared previously by other workers although no detailed analyses of the ^{19}F nmr spectra have been given.

RESULTS AND DISCUSSION

Many methods of preparation for the compound types reported here are known. The most general and convenient is the addition of the organometallic halide to the lithium salt. This salt can almost invariably be prepared from butyllithium and the parent acid. The formation of the lithium salt is most commonly achieved at low temperature, for in the case of a relatively strong acid, such as methanol, the reaction takes place very vigorously at room temperature. Moreover, in the case of the pentafluorophenyl and pentafluoroanilino compounds, the lithium derivative is unstable at room temperature.

e.g. $C_6F_5NH_2 + n\text{-}C_4H_9Li \xrightarrow{-70°} C_6F_5N(H)Li + C_4H_{10}$ [II.1]

$C_6F_5N(H)Li + ClSn(CH_3)_3 \rightarrow C_6F_5N(H)Sn(CH_3)_3 + LiCl$ [II.2]

A reaction which does not fit this pattern precisely is the reaction of pentafluorophenyllithium with dimethyldichlorosilane in 1:1 molar ratio. The expected pentafluorophenyl chloro derivative could not be found but bis(pentafluorophenyl)dimethylsilane was isolated in good yield. This is particularly interesting since a previous attempt to form the disubstituted compound from the pentafluorophenyl Grignard reagent and dichlorodimethylsilane in 2:1 ratio had yielded only polymeric products (54).

In the cases of the alkali metal salts which are stable at room temperature, the formation and use of the sodium salts is as convenient as the lithium salts. Their preparation may be achieved using sodium hydride (55) or sodium ethoxide, e.g.,

$$NaH + C_6H_5OH \longrightarrow NaOC_6F_5 + H_2 \qquad [II.3]$$

$$NaOC_6F_5 + ClSn(C_6H_5)_3 \longrightarrow C_6F_5OSn(C_6H_5)_3 + NaCl \qquad [II.4]$$

Phenoxides may also be prepared from the phenol and organometallic halide by removal of the halogen acid either through boiling or through use of an amine as acid acceptor. Both of the latter methods are reported to give better yields for phenols than for alcohols (56). The latter method has in fact been used by Davidson et al. (57) to prepare $(C_6H_5)_3GeSC_6F_5$. These workers also prepared the analogous lead compound very efficiently from $Pb^{II}(SC_6F_5)_2$ and $(C_6H_5)_3PbCl$.

Of the compounds reported here only two appeared to be unstable over a period of six months. Pentafluoroanilinotrimethyltin became black due to some decomposition, and the corresponding phenoxy-derivative deposited white crystals which are almost certainly polymeric, as shown by their virtual insolubility in common solvents.

Infrared Spectra. Although the spectra were not measured with the degree of accuracy necessary to attempt very precise assignments, they nonetheless proved to be

extremely useful. This was true not only with regard to confirming the structure of the products, but also in showing the absence of starting materials and impurities. The principal peaks of the pure products are shown in Table I.

All compounds exhibit the C-H stretches of methyl and/or phenyl groups which, as expected, occupy the regions 3030-2875 cm^{-1} and 3070-2980 cm^{-1} respectively. The only bands which were observed above these regions are N-H stretches of the anilino derivatives. The Si-H stretch in $(CH_3)_2Si(H)C_6F_5$ occurs at 2165 cm^{-1}, whereas 2180 cm^{-1} is considered an average value for such a vibration (58).

Typical aromatic stretches are observed in the region 1670-1400 cm^{-1} but often cannot be immediately assigned to either phenyl or pentafluorophenyl rings. One band characteristically appears in the region 1665-1640 cm^{-1} (59) for those compounds which have a C_6F_5 group directly attached to silicon. This band must therefore be due to a vibration of the pentafluorophenyl ring perturbed by the central atom. The absorptions between 1460 and 1400 cm^{-1} are observed only in the triphenyl derivatives and are thus assigned to vibrations of the unfluorinated aromatic systems. This is further supported as the $Si-C_6H_5$ moiety characteristically produces a band at approximately

TABLE I

Infrared Spectral Data [a]

Compound	
$C_6F_5Si(CH_3)_3$	2950m, 2895w, 1645, 1505s, 1465vs, 1375s, 1284s, 1252s, 1082vs, 967s, 855vs, 635s.
$C_6F_5Si(CH_3)_2H$	2965m, 2890m, 2165s, 1640s, 1510s, 1465vs, 1375s, 1283s, 1249s, 1080vs, 964s, 889vs, 845s, 657m, 630m, 495m
$C_6F_5Si(CH_3)_2C_6F_5$	2955m, 2895w, 1640s, 1465vs, 1380s, 1290s, 1261s, 1091vs, 968s, 860s, 560m.
$C_6F_5Si(CH_3)_2Br$	2945m 2890w, 1640s, 1510s, 1465vs, 1375s, 1290s, 1259s, 1090vs, 971vs, 863s, 681s, 516s, 489m.
$C_6F_5Si(CH_3)_2OCH_3$	2950m, 2895w, 2830m, 1640s, 1555s, 1460vs, 1375s, 1285s, 1256s, 1188m, 1091vs, 968s, 852vs, 647s.
$C_6F_5Si(CH_3)_2N(CH_3)_2$	2960m, 2890m, 2840m, 2790m, 1640s, 1510s, 1460vs, 1370m, 1281s, 1254s, 1172m, 1081vs, 992s, 965s, 837s, 619m.
$C_6F_5Si(CH_3)_2N(H)C_6H_5$	3400m, 3040m, 2950m, 1640s, 1495s, 1465vs 1380s, 1286s, 1250s, 1172m, 1083vs, 967s, 908m, 853s, 689s, 499s.
$C_6F_5OSi(CH_3)_3$	2955m, 2890vw, 1520vs, 1470m, 1320m, 1260s, 1172s, 1028vs, 991s, 852vs, 756m.

$C_6F_5OGe(CH_3)_3$	2990m, 2920w, 1515vs, 1485s, 1315m, 1248m, 1166s, 1034vs, 991s, 735vs, 674m, 625s.
$C_6F_5OSn(CH_3)_3$[b]	2995m, 1515vs, 1490s, 1311m, 1169s, 1019vs, 993s, 780s, 547m.
$C_6F_5OPb(CH_3)_3$	3030w, 2920w, 1505vs, 1460s, 1163m, 1012vs, 987s, 672m.
$C_6F_5OSi(C_6H_5)_3$	3070m, 3050m, 2995w, 1590m, 1520vs, 1490s, 1435s, 1175m, 1122s, 1030s, 996s, 700s, 518s.
$C_6F_5OGe(C_6H_5)_3$	3070m, 3050m, 2995m, 1510vs, 1470s, 1430s, 1311m, 1159m, 1098s, 1005vs, 740vs, 695s, 462s.
$C_6F_5OSn(C_6H_5)_3$	3060m, 3045m, 1495vs, 1470vs, 1425s, 1310m, 1167s, 1078s, 1003vs, 730vs, 694s, 441s.
$C_6F_5OPb(C_6H_5)_3$	3040m, 3025m, 1495vs, 1460s, 1420s, 1304m, 1161s, 1012vs, 995vs, 690s.
$C_6F_5SSi(CH_3)_3$	2930m, 2875w, 1490vs, 1249s, 1088s, 1017m, 977s, 862s, 626m.
$C_6F_5SGe(CH_3)_3$	2960m, 2900m, 1520s, 1500vs, 1242m, 1092s, 980s, 864s, 614m, 570m.
$C_6F_5SSn(CH_3)_3$	2975w, 2905m, 1500s, 1480vs, 1085s, 977s, 861s, 533m.
$C_6F_5SPb(CH_3)_3$	3000vw, 2920w, 1515s, 1495vs, 1082s, 974s, 860s.

$C_6F_5SSi(C_6H_5)_3$	3060m, 3045m, 2990w, 1485vs, 1425s, 1111s, 1088s, 978s, 859s, 696s.
$C_6F_5SGe(C_6H_5)_3$	3055m, 3040m, 2980w, 1505s, 1485vs, 1430s, 1091s, 978s, 860s, 697s.
$C_6F_5SSn(C_6H_5)_3$	3060m, 3045m, 2980w, 1505s, 1485vs 1425s, 1086s, 1073m, 978s, 859s 696s.
$C_6F_5SPb(C_6H_5)_3$	3070w, 3050vw, 1510s, 1480vs, 1435s, 1083s, 975s, 859s, 691s.
$C_6F_5N(H)Si(CH_3)_3$[b]	3390s, 2950m, 2890w, 1520vs, 1470s, 1395s, 1260s, 1168m, 1025vs, 992s, 851s, 761m.
$C_6F_5N(H)Sn(CH_3)_3$[b]	3355s, 2955m, 2885m, 1520vs, 1475s, 1375s, 1261s, 1247s, 1160m, 1014vs, 980vs, 781s.

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[a] Principal peaks of spectra measured as CCl_4 solutions in 0.5mm KBr cells.

[b] Spectra measured as neat liquid between NaCl plates.

1430 cm^{-1} (60), and other Group IV metal-phenyl systems could be expected to give similar bands. Probably the most characteristic feature of the spectra of all the compounds reported here is an extremely intense band between 1520 and 1460 cm^{-1}, with somewhat less intense bands in the same region. Since it is present in all compounds, it is assigned to a pentafluorophenyl aromatic stretch.

The region 1400-1000 cm^{-1} is dominated by absorptions due to C-F bonds, these absorptions showing their normal high intensity. It is therefore difficult to assign unambiguously any band in this region; in particular, bands are also expected from C_6H_5-M vibrations (61) and from Si-O vibrations. The $SiCH_3$ group typically exhibits bands at 1250 and 840 cm^{-1} (60), and in all the methylsilicon compounds there is a band within 10 cm^{-1} of the higher value. Although the assignment to this group is not without doubt, any other seems unlikely. Further, the lower band can also be accounted for, in all appropriate compounds, by a band between 837 and 863 cm^{-1}.

Finally, at approximately 700 cm^{-1} there is a strong absorption in all triphenyl derivatives; this is typical of ring vibrations.

^{1}H NMR Spectra. The parameters obtained from the measurement of ^{1}H nmr spectra are listed in Table II and some representative spectra are shown in Figures 1-4.

The compounds $(CH_3)_3MOR$ and $(CH_3)_3MSR$, where M is a group IV element and R an organic group are expected, on the basis of previous work (62), to exhibit methyl proton resonances at lower chemical shift for sulfur than for oxygen derivatives. This has been attributed to anisotropy in the metal-sulfur bond (62). The compounds reported here (Table II) do not show this typical order except for the silicon derivatives and even the τ values in these compounds are very similar. This implies that either there is an unusually large deshielding of the methyl protons in $(CH_3)_3MOC_6F_5$ or a large shielding in $(CH_3)_3MSC_6F_5$.

A comparison at the τ value of $(CH_3)_3SiOCH_3$ (62) with that of $(CH_3)_3SiOC_6F_5$ shows a decrease of 0.25 τ units for the methyls directly attached to silicon, whereas in the analogous sulfur compounds the decrease is only 0.11 τ. It thus appears that the C_6F_5 group causes some deshielding and this is greatest for an oxygen compound. These facts can reasonably be attributed to a much greater donation of electrons from oxygen to the ring than from sulfur to the ring, with the resulting increase in the effective electronegativity of the pentafluorophenoxy-group. This would cause the unusually large deshielding of the methyl protons in the oxygen compounds. This electron donation to the ring is in agreement with conclusions reached on the basis of the

TABLE II

^1H N.M.R. Spectral Data[a]

Compound	Chemical shifts (ppm)		Coupling Constants (cps)	
	τ_{CH_3}	τ^b	J_{CH_3-F} [c]	$J_{^{119}Sn-CH_3}$ or $J_{^{207}Pb-CH_3}$
$C_6F_5Si(CH_3)_3$	9.59		1.5	
$C_6F_5Si(CH_3)_2H$[d]	9.54[e]	5.36[f]	1.0	
$C_6F_5Si(CH_3)_2C_6H_5$	9.15		1.6	
$C_6F_5Si(CH_3)_2Br$	9.01		2.0	
$C_6F_5Si(CH_3)_2OCH_3$	9.49	6.47[g]	1.7	
$C_6F_5Si(CH_3)_2N(CH_3)_2$	9.55	7.50[h]	1.7	
$C_6F_5Si(CH_3)_2N(H)C_6H_5$	9.35	6.28	1.7	
$C_6F_5OSi(CH_3)_3$	9.70		0.9	
$C_6F_5OGe(CH_3)_3$[i]	9.37		0.8	
$C_6F_5OSn(CH_3)_3$	9.39			57.8
$C_6F_5OPb(CH_3)_3$	8.49			65.2
$C_6F_5SSi(CH_3)_3$	9.67		0.6	
$C_6F_5SGe(CH_3)_3$	9.43		0.6	
$C_6F_5SSn(CH_3)_3$[j]	9.49			57.0
$C_6F_5SPb(CH_3)_3$	8.64			63.5
$C_6F_5N(H)Si(CH_3)_3$[k]	9.75	6.80[l]	1.4	
$C_6F_5N(H)Sn(CH_3)_3$	9.55	7.02[m]	1.1	58.4

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[a] Measured in $CDCl_3$ solution at 60 Mc.

[b] Refers to methyl attached to nitrogen or oxygen or to a proton

attached to nitrogen or silicon.

[c] No reported value indicates a coupling of < 0.4 cps.

[d] Figure 1.

[e] $J_{HSiCH_3} = 3.9$ cps, $J_{HSi-F} < 0.5$ cps.

[f] Septet, $J_{HSiCH_3} = 3.9$ cps.

[g] $J_{CH_3O-F} = 0.5$ cps.

[h] $J_{CH_3N-F} = 0.9$ cps.

[i] Figure 3.

[j] Figure 4.

[k] Figure 2.

[l] Peak broad in ^1H nmr spectrum, however from ^{19}F nmr spectrum coupling to meta and para fluorines both found $\simeq 0.5$ cps.

[m] Peak broad in ^1H nmr spectrum, however from ^{19}F nmr spectrum $J_{H\text{-meta }F} = 1.0$ cps and $J_{H\text{-para }F} = 0.9$ cps.

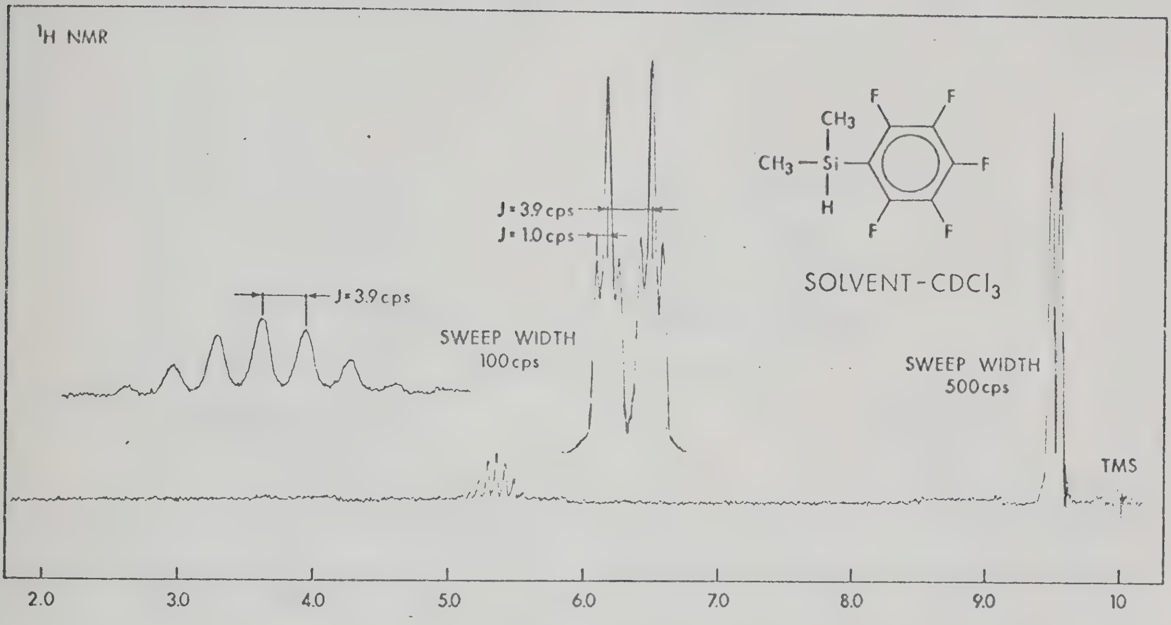

FIGURE 1

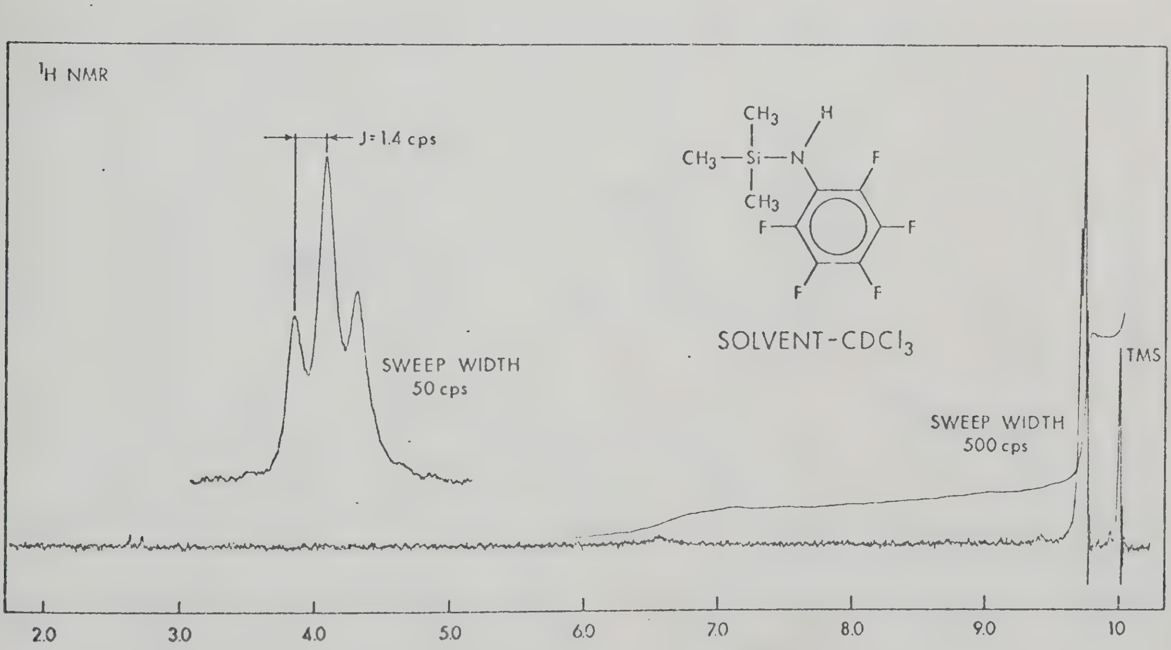

FIGURE 2

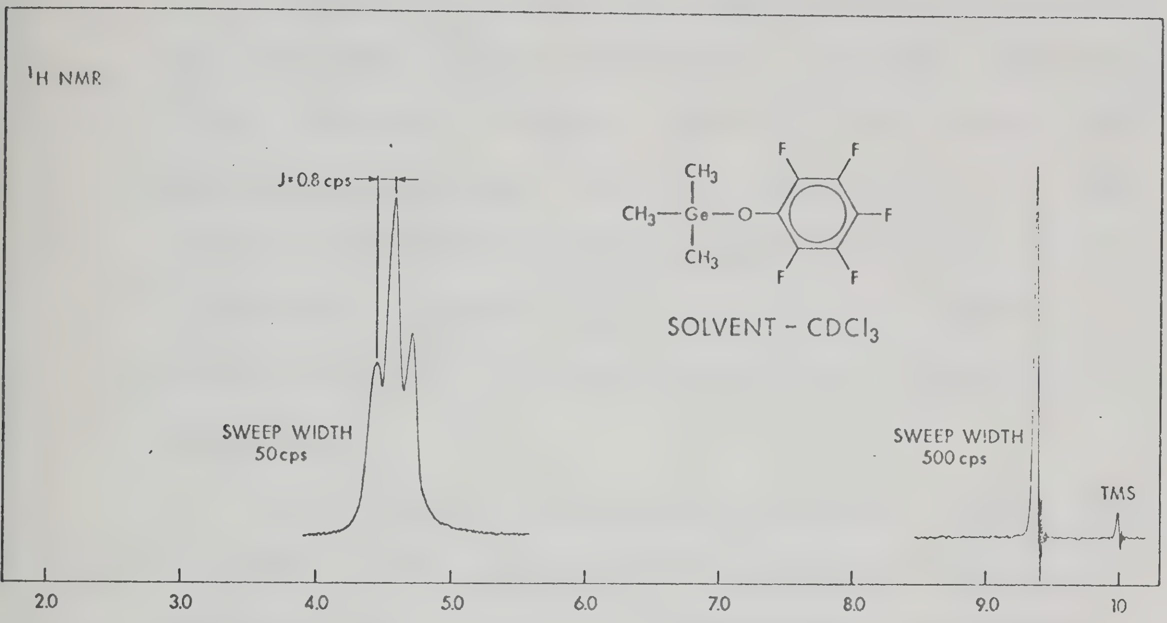

FIGURE 3

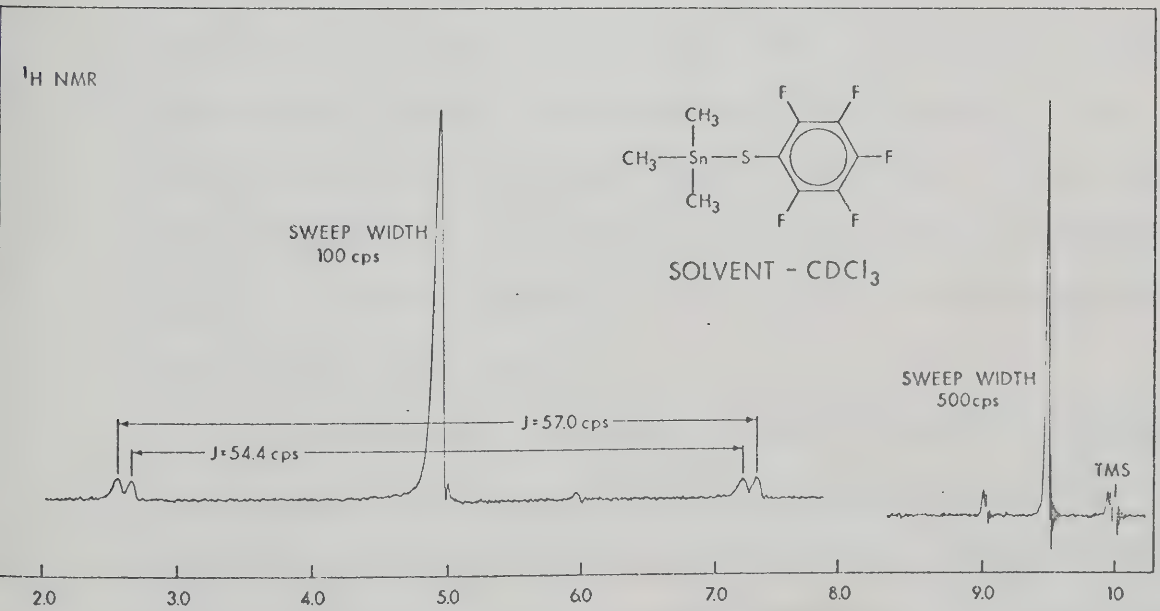

FIGURE 4

^{19}F nmr spectra, discussed below.

Further, the slightly larger couplings of protons to ^{119}Sn and ^{207}Pb in the oxygen compounds, as compared to the sulfur analogues, imply that the oxygen substituent is somewhat the more electronegative. This of course assumes that the coupling is primarily due to the Fermi contact term and that s character is concentrated in the bonds to the more electropositive substituents.

As is to be expected from previous results (62), τ values in the oxygen and sulfur series follow the order Si > Sn > Ge > Pb; considerable uncertainty remains as to the reason for this order (63).

Coupling from ring fluorines to side chain protons has been discussed in detail by Burdon (64). The reasonable suggestion was made that coupling to fluorines substituted in the ortho positions of a phenyl ring takes place by a "through space" mechanism to an extent which depends on the nearness of the protons and fluorines, and to a lesser degree on the relative orientations of the C-H and C-F bonds.

In the series of Table II which result from changing the Group IV element, increasing the atomic number causes a decrease in the coupling constant [e.g. in the series $(CH_3)_3MOC_6F_5$, $J_{CH_3-F} = 0.9$ cps (for M=Si, 0.8 cps (M=Ge), < 0.4 cps (M=Sn or Pb)]. This may be attributed to an increased distance between the methyl protons and o-fluorines which would result from the larger size of

of the Group IV element. A comparison of the coupling, 1.6 cps, in $(C_6F_5)_2Si(CH_3)_2$ with the published value of 0.4 cps for $(C_6F_5)_2Sn(CH_3)_2$ (65) is consistent with the size effect.

Of particular interest are the couplings in the compound $C_6F_5Si(CH_3)_2H$ (Figure 1) where, despite a coupling of 1.0 cps between the methyl protons and o-fluorines, no coupling is observable between the proton on silicon and the o-fluorines. It seems reasonable to suppose that F-H "through space" coupling would take place only when the two atoms can move to within a distance of less than the sum of the Van der Waals radii (i.e. < 2.55 Å) as has been suggested in the case of F-F "through space" coupling (66). Calculations on the compound $C_6F_5Si(CH_3)_2H$ using normal covalent radii and idealised geometry show that the methyl proton to o-fluorine minimum distance is considerably less than 2.55 Å while the silicon proton to o-fluorine distance is greater, thus the observed result is to be expected.

^{19}F NMR Spectra. The parameters obtained from ^{19}F nmr spectra by standard procedures (53) are listed in Tables III and IV and an example of a recorded spectrum is shown in Figure 7. Most important of the parameters are the chemical shift of the p-fluorine (ϕ_p) and the ortho to para coupling constant (J_{24}) since a plot of these two

TABLE III

^{19}F N.M.R. Spectral Data[a]

Compound	ϕ_D[b]	ϕ_p[b]	ϕ_m[b]	$\pm J_{24}$[c]	$\mp J_{34}$	$\mp J_{23}$	$\pm J_{25}$	$\mp J_{35}$	$\mp J_{26}$
$C_6F_5Si(CH_3)_3$[d]	126.5	152.9	162.1	3.3	19.2	23.9	10.7	1.2	4.2
$C_6F_5Si(CH_3)_2H$	127.7	152.0	161.9	3.4	19.1	24.8	10.9	0.9	4.3
$C_6F_5Si(CH_3)_2C_6F_5$	127.4	150.1	161.1	4.2	19.6	24.1	10.6	0.7	4.9
$C_6F_5Si(CH_3)_2Br$	126.8	149.7	161.1	4.8	19.7	23.6	10.4	0.7	5.2
$C_6F_5Si(CH_3)_2OCH_3$	128.0	151.9	161.9	3.8	19.1	24.0	10.9	1.1	4.5
$C_6F_5Si(CH_3)_2N(CH_3)_2$	129.0	153.3	162.1	3.1	19.4	25.3	10.9	1.5	4.4
$C_6F_5Si(CH_3)_2N(H)C_6H_5$	128.2	151.5	161.6	3.9	19.5	24.4	10.7	1.0	4.3
$C_6F_5CH_2Br$	143.3	154.0	162.3	2.1	20.8	22.4	8.9	0.7	3.9
$C_6F_5CH_2COCl$	143.6	153.6	162.2	1.8	20.9	22.2	8.5	1.3	3.9
$C_6F_5CH_2OH$	145.0	155.6	163.1	1.5	20.3	26.1	5.3	2.0	2.0
$C_6F_5OSi(CH_3)_3$[e]	158.7	167.6	165.1	-4.4	21.0				
$C_6F_5OSi(C_6H_5)_3$[e]	156.2	166.5	165.0	-4.3	21.6				
$C_6F_5OGe(C_6H_5)_3$[e]	157.0	169.2	166.3	-5.0	21.6				
$C_6F_5OSn(C_6H_5)_3$[e]	160.4	172.8	168.8	-6.4	21.9				
$C_6F_5OPb(C_6H_5)_3$[e]	161.3	176.1	168.2	-8.0	22.2	25.2	6.0	0	-5.5
$C_6F_5N(H)Si(CH_3)_3$[e]	158.9	174.1	165.7	-7.0	21.4	21.5	4.6	2.7	-3.3

TABLE III (continued)

[a] Obtained from approximately 10 mole % solutions in C_6H_6.

[b] Relative to $CFCl_3$, reference C_6H_6 (chemical shift = 1630.0 ppm) in ppm

[c] The fluorine atoms are labelled by numbering around the ring, those adjacent to the substituent being 2 and 6, values in cps.

[d] Figure 7.

[e] Taken from reference 53.

TABLE IV

p-Fluorine Chemical Shifts (ϕ_p) and o-p-Fluorine Coupling Constant (J_{24})[a]

Compound	ϕ_p[b]	J_{24}[c]	Compound	ϕ_p[b]	J_{24}[c]
$C_6F_5OGe(CH_3)_3$	170.3	-5.6	$C_6F_5SSi(CH_3)_3$	155.3	1.4
$C_6F_5OSn(CH_3)_3$	174.2	-7.3	$C_6F_5SGe(CH_3)_3$	156.5	1.0
C_6F_5OH	171.2	-6.1	$C_6F_5SSn(CH_3)_3$	158.4	0
$C_6F_5N(H)B(C_6H_5)_2$	161.2	-1.3	$C_6F_5SPb(CH_3)_3$	160.0	0
$C_6F_5N(H)CH_3$	173.8	-6.9	$C_6F_5SSi(C_6H_5)_3$	155.7	1.8
$C_6F_5N(H)Si(CH_3)_3$	174.1	-7.0	$C_6F_5SGe(C_6H_5)_3$	156.5	1.7
$C_6F_5NH_2$	174.3	-7.0	$C_6F_5SSn(C_6H_5)_3$	158.1	1.1
$C_6F_5N(H)Sn(CH_3)_3$	179.5	-9.2	C_6F_5SH	159.1	0

[a] Reference 53

[b] Relative to $CFCl_3$ in ppm, reference C_6F_6 (chemical shift = 163.0 ppm).

[c] In cps.

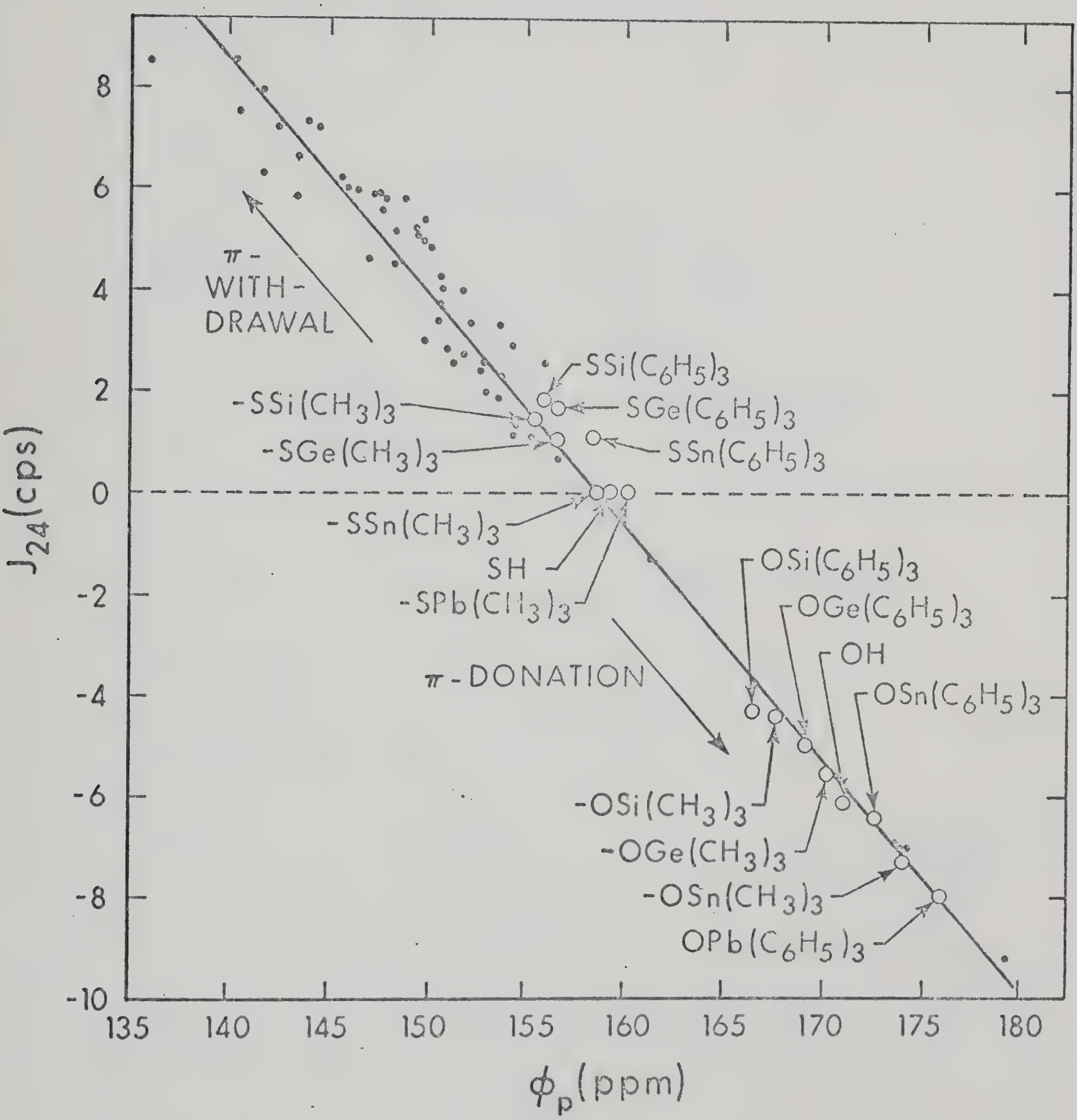

FIGURE 5. The J_{24} - ϕ_p relationship for compounds of the type C_6F_5-XMR_3 where X=0 or S, M=Si, Ge, Sn and Pb, R= CH_3 or C_6H_5.

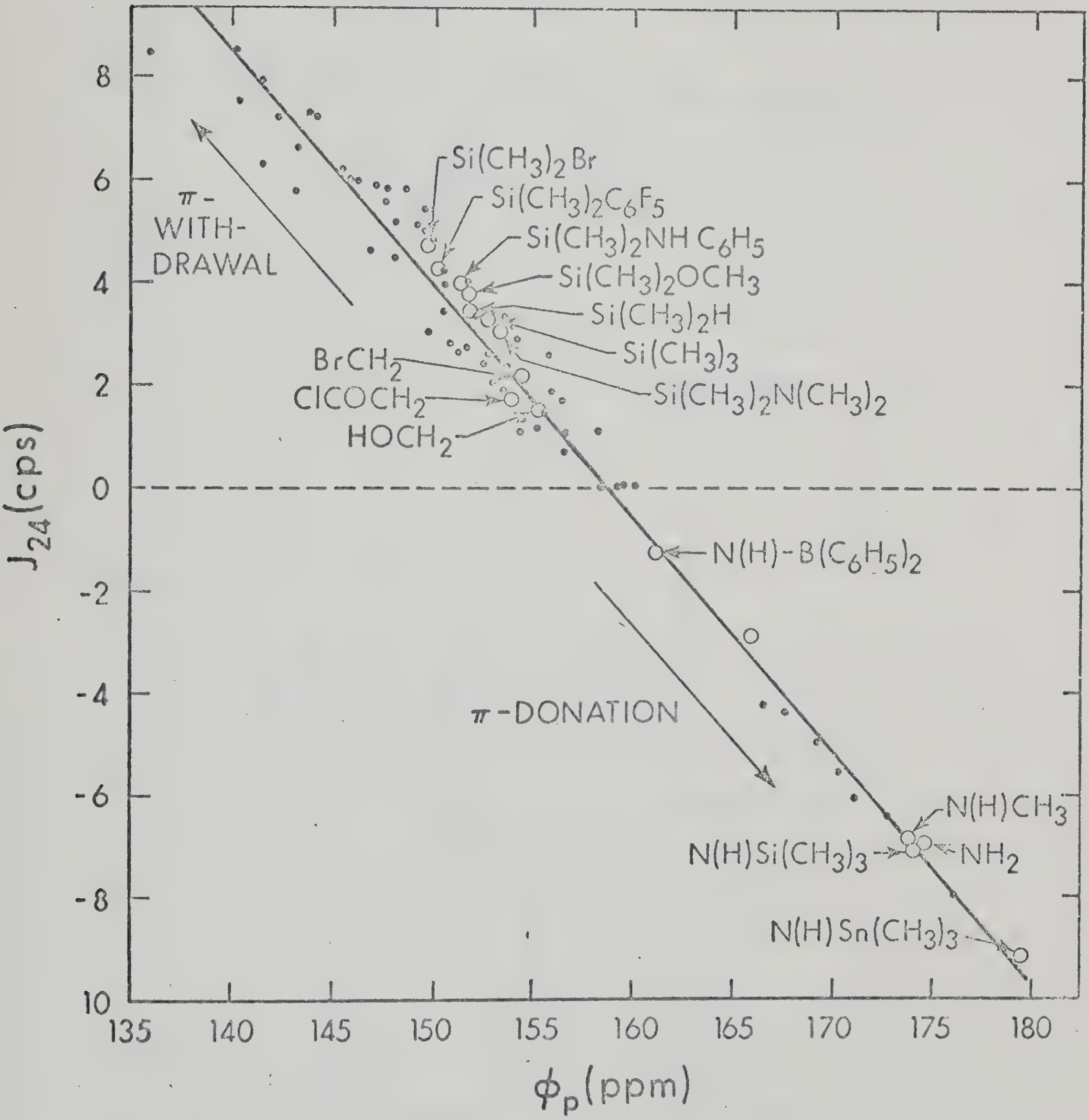

FIGURE 6. The J_{24} - ϕ_p relationship for some pentafluorobenzyl and pentafluoroaniline derivatives and the compounds $C_6F_5(CH_3)_2SiX$ where X = H, CH_3, C_6H_5, OCH_3, $N(CH_3)_2$ or $N(H)C_6H_5$.

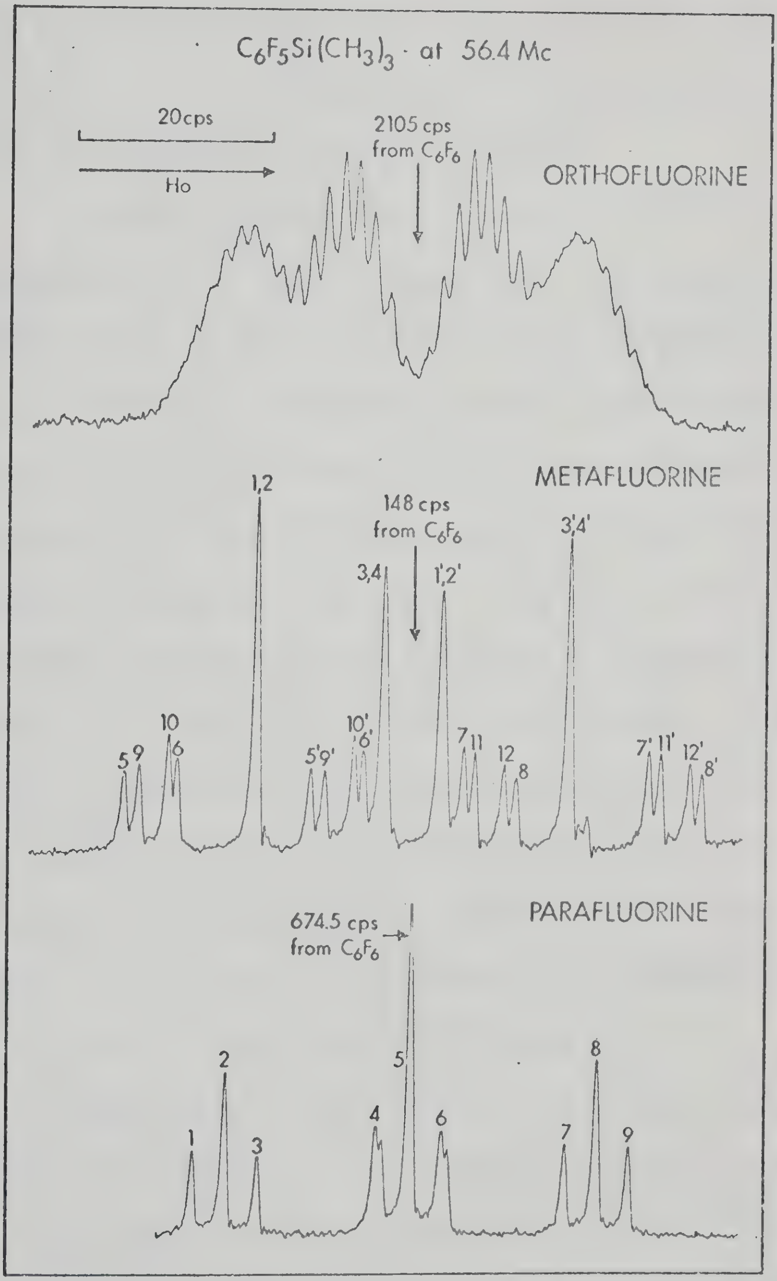

FIGURE 7. The ^{19}F nmr spectrum of $C_6F_5Si(CH_3)_3$.

factors has been shown to reveal electron interactions with the pentafluorophenyl system (50,51,52,53). Hence only ϕ_p and J_{24} were measured for some compounds (53), Table IV. Plots resulting from the compounds reported here are shown in Figures 5 and 6.

Oxygen appears from Figure 5 to be a strong donor, presumably by a $(p \to p)\pi$ donation. In analogous compounds, sulfur shows a net π effect close to zero since any donor effect is counterbalanced by donation of ring π electrons to the vacant 3d orbitals of sulfur. The lone pairs on sulfur and oxygen are expected to have two possible modes of bonding: they can interact with the pentafluorophenyl group causing an increase in π electron density in the ring, or with the Group IV element, except carbon, decreasing ring π-electron density. Thus the two competing bonding possibilities will have opposite effects on the pentafluorophenyl ring, which provide a means of estimating the extent of π bonding of oxygen or sulfur to the Group IV element.

The order of the Group IV elements appears from Figure 5 to be the same in both oxygen and sulfur series, and indicates that the tendency to form π bonds with oxygen (or sulfur) decreases in the series Si > Ge > Sn > Pb. A possible explanation of this would be that the overlap between the Group IV vacant d orbital and the Group VI lone pairs is strongest for silicon and decreases to lead. Attempts to prepare the trimethyl-

carbon (t-butyl) derivatives were not successful. These points would be extremely valuable since they would represent cases in which double bond formation by the Group VI element was possible only with the benzene ring. The points for the phenol and thiophenol (53) are available, however, and their positions within the two series are of some interest. The phenol derivative is midway between germanium and tin, which would indicate that while silicon and germanium are π acceptors, tin and lead are π donors relative to hydrogen.

These estimates of the π-acceptor properties of the Group IV elements are in general accord with conclusions reached by other workers (16,17,67). The published studies consisted of observing the base strengths of Group IV element derivatives of nitrogen, oxygen or sulfur with respect to a reference acid. Base strengths are of course reduced when there is delocalisation of the lone pairs of nitrogen, oxygen or sulfur into the Group IV element d orbitals. Thus silylamines were observed to be weak bases whereas aminotin compounds were strong, in fact stronger than simple organic amines.

The electron donating properties of tin and lead have been explained in terms of electronegativities and inductive effects. In the light of this study, however, it may well be possible that tin and lead are exhibiting π-donor properties.

For the sulfur compounds, the thiophenol appears

close to tin and lead derivatives (Figure 5) and silicon and germanium again act as π-acceptors. Thus the π-acceptor properties of germanium seem stronger with sulfur than with oxygen, which also agrees with previous studies (17).

The J_{24} and ϕ_p values of several pentafluoroaniline derivatives are shown graphically in Figure 6, with positions indicating some donation of the nitrogen lone pair to the pentafluorophenyl ring. Replacement of hydrogen in pentafluoroaniline by a group capable of π-bonding with nitrogen should reduce donation to the pentafluorophenyl ring. In the series C_6F_5-N(H)R, π donation by R to the pentafluorophenyl ring increases in the order $B(C_6H_5)_2 < CH_3 \sim Si(CH_3)_3 \sim H < Sn(CH_3)_3$. The expected nitrogen to boron (p→p) π bonding in the boron compound reduces the donation of the lone pair to the pentafluorophenyl ring. Since no change in the J_{24} and ϕ_p values is found when one of the protons of aniline is substituted by either a methyl or trimethylsilyl group, it is concluded that there is no appreciable π character in the nitrogen-silicon bond in N-trimethylsilylpentafluoroaniline. These results are in contrast to some other studies of Si-N bonding (Chapter I) and also in contrast to the analogous oxygen and sulfur compounds.

The above discussion uses the pentafluorophenyl group as a test ligand attached to the more electronegative

atom of a bond between a Group IV metal and oxygen, sulfur or nitrogen. It seemed appropriate to confirm the results, particularly the interesting results with a silicon-nitrogen bond, by attaching the pentafluorophenyl group directly to the metal. Thus the series of compounds $C_6F_5(CH_3)_2SiX$ (X = H, CH_3, C_6F_5, OCH_3, $N(CH_3)_2$ or $N(H)C_6H_5$) was prepared and the resulting J_{24} and ϕ_p values are shown graphically in Figure 6. The major factor governing the positions on this plot is considered to be the ability of silicon to withdraw π-electron density from the aromatic ring to its own d orbitals (18,68,69). The minor changes within the series, somewhat surprisingly, do not show a dependence on the π-bonding ability of the group X and appear to reflect the electronegativity of X. A small increase in J_{24} thus results from an electronegative substituent on silicon. This is further confirmed by a change in the τ values of the methyl groups on silicon (Table II) in almost exactly the same order as the change in J_{24}; low τ values are usually associated with electronegative substituents.

It is thought that only σ inductive (electronegativity) effects are transmitted from a substituent, Z, to the aromatic system in a benzyl compound $C_6H_5CH_2Z$. Then from the above discussion the compounds $C_6F_5(CH_3)_2SiX$ may be considered as similar to pentafluorobenzyl derivatives. Spectral data for those pentafluorobenzyl compounds which are commercially available is shown in Table III and Figure 6. The plot of J_{24} vs ϕ_p indicates that the

substituents (-OH,-COCl,-Br) on the benzyl derivatives are electron withdrawing relative to hydrogen (in $C_6F_5CH_2H$ (53), $\phi_p = 159.1$, $J_{24} = 0$). The -OH group is a good π-donor when directly attached to a perfluoro-aromatic system, however its apparent withdrawing ability can be rationalised by its σ-inductive electronegativity effect which would be expected to be dominant in this benzyl derivative. Presumably the σ inductive effect is mainly responsible for the withdrawing ability of the -COCl and -Br groups although these groups are expected to be withdrawing by both σ and π mechanisms.

EXPERIMENTAL

All reactions were carried out under anhydrous conditions with a nitrogen atmosphere. Hydrocarbon solvents were dried over sodium wire or 9.5% sodium/lead alloy. Anhydrous diethyl ether was used as obtained from commercial sources and tetrahydrofuran was dried by distillation from lithium aluminum hydride.

Fractionation were normally carried out in vacuum-jacketed Vigreux columns, fitted with a modified Perkin Triangle when reduced pressure was used. In those cases where a second fractionation was necessary, a concentric tube column was employed.

Methods reported in the literature were used to prepare bromotrimethylgermane (70), trimethyllead-bromide (71), bromotriphenylgermane (72), and triphenyllead chloride (73). Other reagents are available commercially and were used without further purification.

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany and by the microanalytical laboratory of this department with results given in Table VI. A Spencer 1241 refractometer was used to determine the refractive indices (Table V). Infrared spectra were measured on a Perkin-Elmer Model 337 (grating) spectrometer with a polystyrene film as reference. Proton and fluorine magnetic resonance spectra were obtained with a Varian A56/60A spectrometer and mass spectra were recorded using an A.E.I. M.S.9 instrument.

Method A.

Preparation of $C_6F_5Si(CH_3)_3$. A solution of n-butyl lithium in hexane (31.3 ml, 47 mmol) was added slowly to a solution of pentafluorobenzene (7.8 g, 47 mmol) in 40 ml of anhydrous diethylether. The mixture was warmed to -10°, stirred for 30 min and cooled again to -70°. Trimethylchlorosilane (5.1 g, 47 mmol) was added slowly and the mixture allowed to attain room temperature. The precipitate of lithium chloride was filtered off and solvent stripped off under vacuum. The remaining liquid was fractionated to give pentafluorophenyltrimethylsilane (b.p. 179°/593 mm, 7.4 g, 31 mmol).

By the same method $C_6F_5Si(CH_3)_2H$ was prepared from dimethylchlorosilane. The compound $(C_6F_5)_2Si(CH_3)_2$ was also prepared in this way using 1:1:1 molar ratios of pentafluorobenzene, n-butyl lithium and dimethyldichlorosilane.

Method B.

Preparation of $C_6F_5Si(CH_3)_2Br$. To pentafluorophenyldimethylsilane (8.68 g, 38 mmol) in 20 ml of pentane, bromine (6.0 g, 38 mmol) was added very slowly in 30 ml of the same solvent. The solution was stirred for 1 hr, after which time the bromine color had virtually disappeared. Pentane was pumped off under vacuum and the less volatile liquid fractionated under reduced pressure to yield 83% of product (b.p. 56°/1.0 mm).

Method C.

Preparation of $C_6F_5Si(CH_3)_2OCH_3$. Methanol (1.07 g, 34 mmol) was mixed with 30 ml of pentane and 13.4 ml of a 2.5M solution of n-butyl lithium (34 mmol) in hexane was added very slowly at -70°. After stirring for 15 min, pentafluorophenyldimethylbromosilane (10.2 g, 34 mmol) was added and the mixture allowed to attain room temperature. Lithium bromide was filtered off after 30 min and solvent removed under reduced pressure. The remaining liquid was fractionated to give the product (b.p. 45°/2.0 mm, 6.2 g, 24 mmol).

The compound $C_6F_5Si(CH_3)_2N(H)C_6H_5$ was produced in the same way using aniline in place of methanol.

Method D.

Preparation of $C_6F_5Si(CH_3)_2N(CH_3)_2$. To a solution of pentafluorophenyldimethylbromosilane (17.5 g, 57 mmol) in 50 ml of pentane was added 10 ml of dimethylamine (158 mmol) at -70°. The mixture was allowed to reach room temperature and was stirred for 30 min while excess amine evaporated. The amine salt was removed by filtration, pentane stripped off under vacuum and the residual liquid distilled under reduced pressure. The product was collected at 49°/1.2 mm in 69% yield.

Method E.

Preparation of $C_6F_5OSi(CH_3)_3$. Pentafluorophenol (12.1 g, 68 mmol) and trimethylchlorosilane (7.4 g, 70 mmol) were refluxed together for 20 hr. The resulting liquid was

fractionated twice under reduced pressure to afford the product in 32% yield.

Method F.

Preparation of $C_6F_5OSn(CH_3)_3$. Sodium pentafluorophenoxide was required for this preparation and was formed in the following way. Clean, dry sodium (1.11 g, 48 mmol) was placed in 50 ml of THF and ethanol (5 ml, 86 mmol) was added carefully. When no metallic sodium remained, pentafluorophenol (8.95 g, 49 mmol) in 10 ml of THF was added. This mixture was refluxed for 30 min and all solvent removed under vacuum. The remaining white solid was washed twice with pentane to yield moderately pure anhydrous sodium pentafluorophenoxide (8.2 g, 40 mmol, m.p. 318° (decomp)).

To a solution of trimethyltin chloride (2.5 g, 12 mmol) in 25 ml of benzene was added sodium pentafluorophenoxide (3.0 g, 15 mmol) dissolved in 25 ml of THF. The mixture was refluxed for 1 hr, allowed to cool, and the precipitate of sodium chloride filtered off. The filtrate was evaporated until only a viscous liquid remained. This liquid was fractionated under reduced pressure to give the product at 70°/0.7 mm.

The analogues $C_6F_5OGe(CH_3)_3$ and $C_6F_5OPb(CH_3)_3$ were prepared in the same manner starting from the appropriate trimethylbromo compound. Pentafluorophenoxytrimethyl lead was purified by recrystallisation from benzene.

Method G.

Preparation of $C_6F_5OGe(C_6H_5)_3$. A solution of pentafluorophenol (1.68 g, 9.1 mmol) in 10 ml of benzene was added to triphenylbromogermane (3.5 g, 9.1 mmol) in 30 ml of the same solvent. To this was added slowly triethylamine (1.27 ml, 9.1 mmol) in 10 ml of benzene. The resulting mixture was refluxed for 4 hr, filtered and the filtrate evaporated to dryness. The residue was recrystallised twice from pentane to yield pure pentafluorophenoxytriphenylgermane (2.95 g, 6.1 mmol).

Similarly $C_6F_5OSi(C_6F_5)_3$ was prepared from the corresponding chlorosilane using pyridine in place of triethylamine.

Method H.

Preparation of $C_6F_5OSn(C_6H_5)_3$. A 49% oil dispersion of sodium hydride (0.75 g, 15 mmol) was washed twice with pentane, dried with a stream of nitrogen, and 7 ml of THF added. Pentafluorophenol (2.5 g, 14 mmol) in 25 ml of THF was added dropwise to the hydride. The mixture was warmed for 10 min and treated with triphenyltin chloride (5.2 g, 14 mmol) in 15 ml of THF. After refluxing for 4 hr and cooling to room temperature, the fine precipitate of sodium chloride which had formed was filtered off and the filtrate evaporated to dryness. The remaining solid was recrystallised twice from pentane to yield the pure product (4.05 g, 7 mmol).

In the case of $C_6F_5OPb(C_6H_5)_3$ prepared in this way, separation from $(C_6H_5)PbCl$ was found to be very difficult. It was best achieved by several recrystallisations from chloroform solution.

Method I.

Preparation of $C_6F_5SSi(CH_3)_3$. Pentafluorothiophenol (4.2 ml, 37 mmol) in 10 ml of diethyl ether was added to 23.8 ml of 1.55M n-butyl lithium (37 mmol) in hexane at -70°. The mixture was allowed to attain room temperature and refluxed for 20 min. Trimethylchlorosilane (4.71 ml, 37 mmol) in 10 ml of diethyl ether was added and the mixture again refluxed for 20 min. After filtration and removal of solvent from the filtrate at reduced pressure, the resulting pale yellow liquid was fractionated at low pressure. The required product was obtained as a colorless liquid (b.p. 53°/0.2 mm, 2.5 g, 9.2 mmol).

All other pentafluorothiophenoxy-derivatives were obtained by methods very similar to this. However, trimethyllead and all the triphenyl compounds were purified by recrystallisation from pentane; the only exception to this was $C_6F_5SPb(C_6H_5)_3$ for which acetone was found most useful.

Method J.

Preparation of $C_6F_5N(H)Sn(CH_3)_3$. To a 1.5M solution of n-butyl lithium (26.7 ml, 40 mmol) in hexane at 70° was

was added pentafluoroaniline (7.32 g, 50 mmol) in 40 ml of diethyl ether. The mixture was allowed to attain 0°, at which temperature slight decomposition begins. Trimethyltin chloride (7.97 g, 40 mmol) in 30 ml of diethyl ether was added quickly. After refluxing for 3 hr, filtering and stripping off the solvent from the filtrate, the remaining liquid was fractionally distilled. At 75°/0.4 mm the pure product (10.5 g, 30 mmol) was obtained.

The analogous silicon compound $\underline{C_6F_5N(H)Si(CH_3)_3}$ was prepared by a similar procedure.

Also prepared by this method from diphenylboron chloride was $\underline{C_6F_5N(H)B(C_6H_5)_2}$ but since this product is a very viscous liquid and difficult to distil the compound could not be obtained analytically pure. Found C = 63.71%, H = 4.17%, Calculated C = 62.29%, H = 3.20%. The product appeared pure by ^1H and ^{19}F nmr spectroscopy, and its identity was confirmed mass spectrometrically (measured mass of molecular ion, 347.0902; calculated mass 347.0903).

TABLE V

Physical Properties and Synthetic Methods

Compound	mp[a] or bp	n_D^{25}	Method	Yield
$C_6F_5Si(CH_3)_3$	170°/693 mm[b]	1.4317[c]	A	66%
$C_6F_5Si(CH_3)_2H$	157°/685 mm	1.4296	A	60%
$C_6F_5Si(CH_3)_2C_6F_5$	79°/0.3 mm	1.4611	A	70%
$C_6F_5Si(CH_3)_2Br$	56°/1.0 mm	1.4643	B	83%
$C_6F_5Si(CH_3)_2OCH_3$	45°/2.0 mm	1.4300	C	71%
$C_6F_5Si(CH_3)_2N(CH_3)_2$	49°/1.2 mm	1.4448	D	69%
$C_6F_5Si(CH_3)_2N(H)C_6H_5$	114°/1.2 mm	1.5134	C	54%
$C_6F_5OSi(CH_3)_3$	56°/7.5 mm	1.4138	E	32%
$C_6F_5OGe(CH_3)_3$	41°/0.6 mm	1.4402	F	38%
$C_6F_5OSn(CH_3)_3$	70°/0.7 mm	1.4767	F	67%
$C_6F_5OPb(CH_3)_3$	mp 161-163°		F	46%
$C_6F_5OSi(C_6H_5)_3$	mp 95-97°		G	73%
$C_6F_5OGe(C_6H_5)_3$	mp 99-100°		G	67%
$C_6F_5OSn(C_6H_5)_3$	mp 73-75°		H	52%
$C_6F_5OPb(C_6H_5)_3$	mp 136-137°		H	9%
$C_6F_5SSi(CH_3)_3$	53°/0.2 mm	1.4688	I	25%
$C_6F_5SGe(CH_3)_3$	52°/0.5 mm	1.4920	I	53%
$C_6F_5SSn(CH_3)_3$	64°/0.3 mm[d]	1.5238	I	22%
$C_6F_5SPb(CH_3)_3$	mp 32°		I	37%
$C_6F_5SSi(C_6H_5)_3$	mp 91-92°		I	43%
$C_6F_5SGe(C_6H_5)_3$	mp 97-99°[e]		I	60%
$C_6F_5SSn(C_6H_5)_3$	mp 84°		I	44%

TABLE V (continued)

$C_6F_5SPb(C_6H_5)_3$	mp	95-96°[f]		I	8%
$C_6F_5N(H)Si(CH_3)_3$		45°/0.8 mm	1.4470	J	55%
$C_6F_5N(H)Sn(CH_3)_3$		75°/0.4 mm	1.4949	J	76%

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[a] All melting points determined using Kofler hot stage microscope.

[b] Lit: bp. 60°/14 mm (54), 170-172° (74), 165° (75), 56°/9.0 mm (76).

[c] Lit: n_D^{22} 1.4331 (75), n_D^{25} 1.4307 (76).

[d] Lit: bp. 62°/0.001 mm and n_D^{20} 1.5244 (77).

[e] Lit: mp. 96-97° (57).

[f] Lit: mp. 95-96° (57).

TABLE VI

Analytical Data

Compound	Analyses					
	Calcd			Found		
	C	H	F	C	H	F
$C_6F_5Si(CH_3)_3$	45.0	3.8		45.1	3.8	
$C_6F_5Si(CH_3)_2H$	42.5	3.1	42.0	42.5	3.1	41.8
$C_6F_5Si(CH_3)_2C_6F_5$	42.9	1.5		43.3	1.9	
$C_6F_5Si(CH_3)_2Br$	31.5	2.0		32.2	1.9	
$C_6F_5Si(CH_3)_2OCH_3$	42.2	3.5	37.1	41.7	3.3	36.3
$C_6F_5Si(CH_3)_2N(CH_3)_2$	44.6	4.8		44.8	4.8	
$C_6F_5Si(CH_3)_2N(H)C_6H_5$	53.0	4.1		53.2	4.2	
$C_6F_5OSi(CH_3)_3$	42.2	3.5	37.1	42.4	3.6	37.1
$C_6F_5OGe(CH_3)_3$	35.9	3.0	31.6	36.1	3.1	31.6
$C_6F_5OSn(CH_3)_3$	31.2	2.6	27.4	32.3	2.7	27.8
$C_6F_5OPb(CH_3)_3$	24.8	2.1		25.0	2.1	
$C_6F_5OSi(C_6H_5)_3$	65.2	3.4	21.5	65.1	3.4	21.4
$C_6F_5OGe(C_6H_5)_3$	59.2	3.1	19.5	59.3	3.2	19.5
$C_6F_5OSn(C_6H_5)_3$	54.1	2.8	17.8	54.4	3.5	17.7
$C_6F_5OPb(C_6H_5)_3$	46.5	2.4	15.2	46.5	2.6	15.4
$C_6F_5SSi(CH_3)_3$	39.7	3.3	34.9	39.8	3.5	34.6
$C_6F_5SGe(CH_3)_3$	34.1	2.9	30.0	34.0	2.9	30.1
$C_6F_5SSn(CH_3)_3$	30.3	2.5	26.2	30.0	2.6	25.6
$C_6F_5SPb(CH_3)_3$[a]	24.0	3.4	21.0	24.6	2.1	23.4
$C_6F_5SSi(C_6H_5)_3$	62.9	3.3	20.7	62.9	3.6	20.7
$C_6F_5SGe(C_6H_5)_3$	57.3	3.0	18.9	57.1	3.2	18.8
$C_6F_5SSn(C_6H_5)_3$	52.5	2.8		52.6	3.0	
$C_6F_5SPb(C_6H_5)_3$	45.2	2.4	14.9	45.6	2.5	15.4

TABLE VI (continued)

$C_6F_5N(H)Si(CH_3)_3$	42.3	4.0	37.2	42.6	4.1	37.0
$C_6F_5N(H)Sn(CH_3)_3$	31.3	2.9	27.2	31.4	3.0	27.3

[a] Confirmed by exact mass measurement of parent ion; calculated mass 452.0111, measured mass 452.0109.

CHAPTER III

THE REACTION OF LIGANDS WITH PENTAFLUOROPHENYLMANGANESE PENTACARBONYL

The use of ^{19}F nmr spectra in studying π-electronic interactions in the pentafluorophenyl group has been demonstrated in Chapter II. It seemed that this method might further be applied to the study of π-bonding in metal carbonyls and the carbonyl stretching frequencies should provide an alternate means of gauging π-effects. With this idea in mind a number of pentafluorophenylmanganese pentacarbonyl derivatives have been prepared and studied by infrared and ^{19}F nmr spectroscopy. The findings proved to be in general agreement with conclusions reached by Stewart and Treichel (78) from a comprehensive study of the analogous monofluorophenyl compounds.

RESULTS AND DISCUSSION

Starting from manganese pentacarbonyl bromide, pentafluorophenylmanganese pentacarbonyl has been prepared by two groups using somewhat different methods (79,80). An adaptation of both procedures was used for this study. The ease of formation of pentafluorophenyllithium (Chapter II) makes it most convenient for reaction with manganese pentacarbonyl bromide. For efficient purification, chromatography on alumina and subsequent

vacuum sublimation consistently gives yields of product in excess of 60%. The compound is white when absolutely pure, but discolors slowly.

Recently an "improved" method of synthesis has been reported (81). This involved the reaction of manganese pentacarbonyl anion with bromopentafluorobenzene to afford $C_6F_5Mn(CO)_5$ in 47% yield. Rausch (80) had prepared this same compound in 47% yield some seven years earlier.

Substitution of pentafluorophenylmanganese pentacarbonyl by various ligands has been achieved by treatment with free ligand, usually with the assistance of heat or ultraviolet light. As would be expected, the substitution reactions resemble those of other manganese pentacarbonyl systems, particularly the phenyl and bromo-derivatives. An exception is the reaction of triphenylphosphite, in which only a monosubstituted derivative is formed even when heat and excess ligand are used. This feature is analogous to the reaction of the monofluorophenyl compound with triphenylphosphite (78). Disubstituted triphenylphosphite complexes are easily obtained in the cases of $Mn(CO)_5Br$ (82) and $Mn(CO)_5C_6H_5$ (83,84).

Infrared Spectra. In the monosubstituted complexes the patterns of the terminal carbonyl stretching frequencies (Table VIII, Figures 8-11) are very similar to those reported for the compounds *cis*-$BrMn(CO)_4L$ (85), *cis*-$C_6H_5Mn(CO)_4L$ (83,86), and *cis*-$FC_6H_4Mn(CO)_4L$ (78),

TABLE VII

Physical Properties and Infrared Spectral Data

Compound	m.p.[a]	Color	Yield	Carbonyl Stretching Frequencies[b]
$C_6F_5Mn(CO)_5$	123-124[c]	white	65%	2131m, 2066vw, 2043vs 2012s, 1968vw[d]
$C_6F_5Mn(CO)_4P(n\text{-}C_4H_9)_3$		pale yellow	12%	2080m, 2011s, 1994vs, 1957s
$C_6F_5Mn(CO)_4P(C_6H_5)_3$	135-137	pale yellow	66%	2084m, 2012m, 2001s, 1959m
$C_6F_5Mn(CO)_4As(C_6H_5)_3$	133-136	pale yellow	54%	2084m, 2011m, 2002s, 1961m
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$	133-134	yellow	51%	2080m, 2011m, 1999s, 1962m
$C_6F_5Mn(CO)_4P(OC_6H_5)_3$	119-121	white	80%	2095m, 2030s, 2015s, 1982s
$C_6F_5Mn(CO)_4NC_5H_5$	105-106	yellow	9%	2090m, 2004vs, 1961s
$C_6F_5Mn(CO)_3[P(n\text{-}C_4H_9)_3]_2$	110-111	pale yellow	38%	2021w, 1935vs, 1903s
$C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$	75-76	white	80%	2050m, 1968vs, 1939s
$C_6F_5Mn(CO)_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$	200(dec)	white	72%	2022s, 1960m, 1926w
$C_6F_5Mn(CO)_3(CH_3SCH_2CH_2SCH_3)$	169-171	yellow	57%	2028m, 1959m, 1914m

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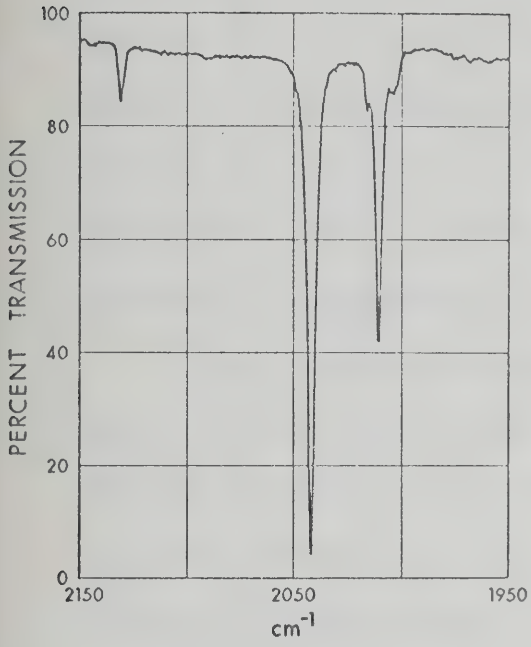
[a] All melting points determined using a Kofler hot stage microscope

[b] Measured in cyclohexane solution

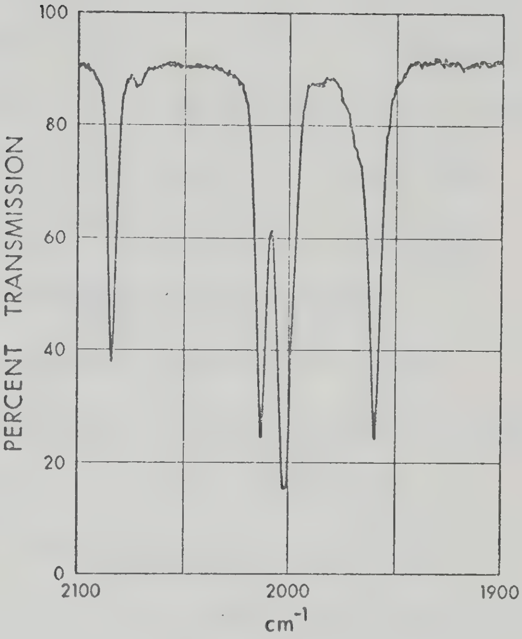
[c] Lit: 118-120 (79); 121-122 (80).

[d] Lit: 2135m, 2068w, 2040vs, 2012s, 1968w in cyclohexane solution (79), 2137, 2053, 2000, 1969 in KBr pellet (80).



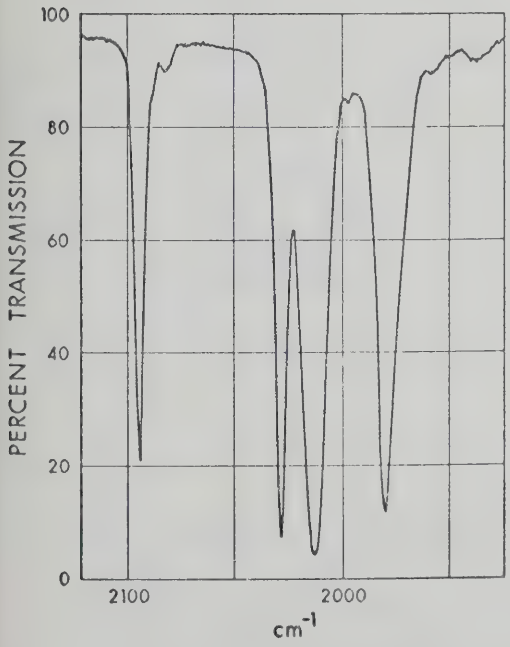
$C_6F_5Mn(CO)_5$

FIGURE 8



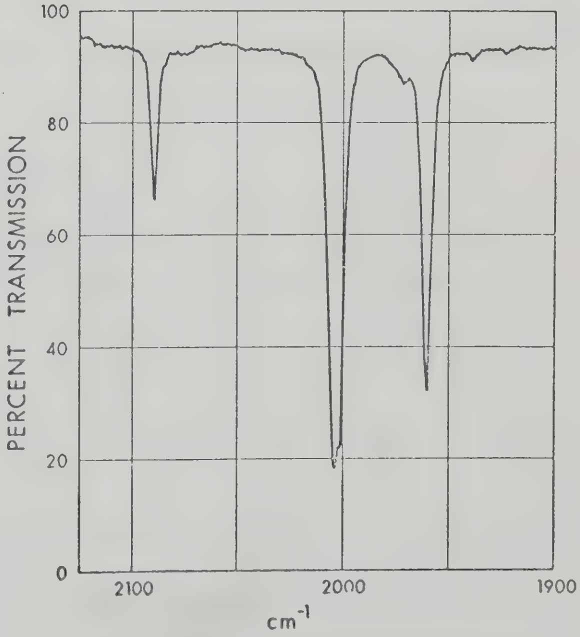
$C_6F_5Mn(CO)_4P(C_6H_5)_3$

FIGURE 9



$C_6F_5Mn(CO)_4P(OC_6H_5)_3$

FIGURE 10

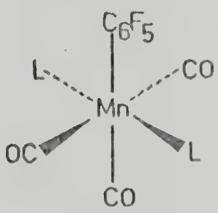


$C_6F_5Mn(CO)_4NC_5H_5$

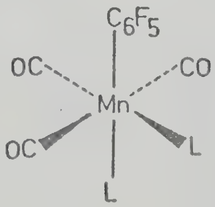
FIGURE 11

suggesting that the pentafluorophenyl group and substituting ligand (L) are also *cis*-to each other. During the preparation of these derivatives (with the exception of L = pyridine), an additional strong infrared band was observed, presumably due to the formation of some *trans* species. Attempts to isolate such species were unsuccessful.

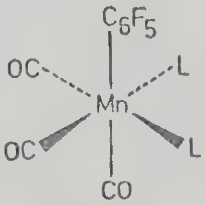
The bis-substituted derivatives are of two types: those having one bidentate ligand and those having two monodentate ligands. This division is evidenced in the spectra (Figures 12-15). The infrared spectra of the bistri-n-butylphosphine and bistriethylphosphite derivatives show a close resemblance to those observed for $Mn(CO)_3L_2Br$ (82), where it was concluded that the donor ligands were mutually *trans*. Thus it may be supposed that a similar arrangement is present in the derivatives reported here (V).



V

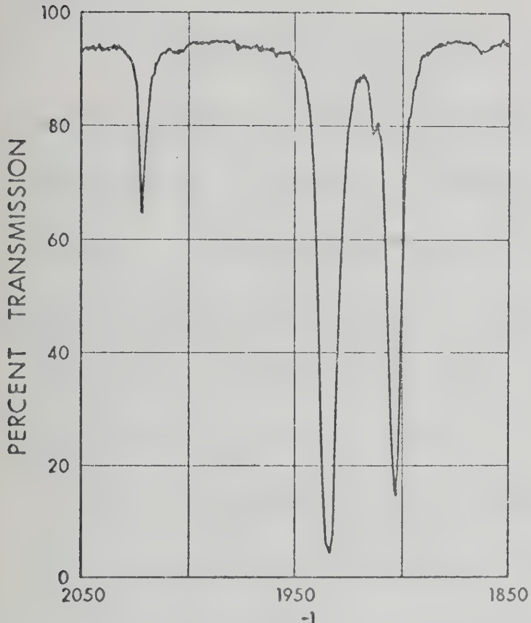


VI



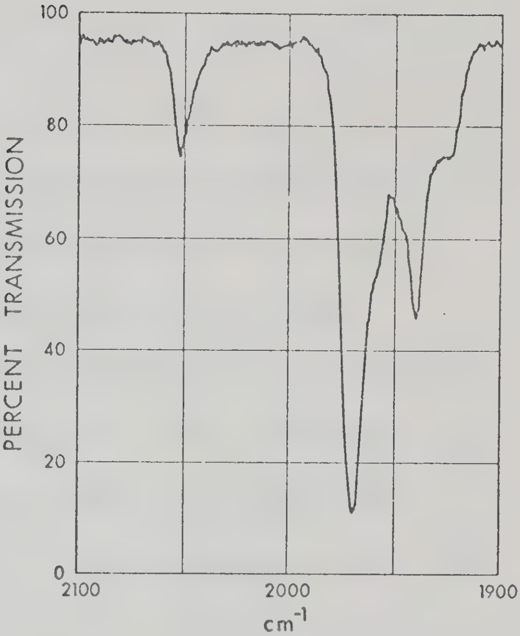
VII

The intensity pattern (weak, strong, strong, in order of decreasing frequency) does not exclude an arrangement in which one phosphorus ligand is *trans* to the pentafluorophenyl group (VI); however, such an arrangement is unlikely in view of the magnetic equivalence of the two phosphorus



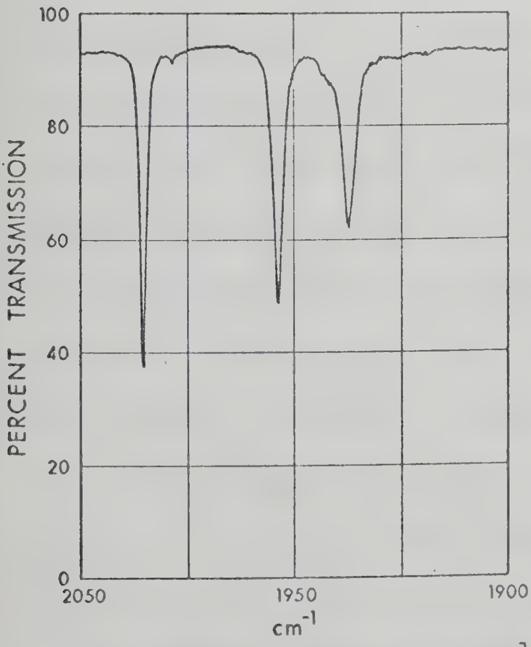
$C_6F_5Mn(CO)_3\,[P(n\text{-}C_4H_9)_3]_2$

FIGURE 12



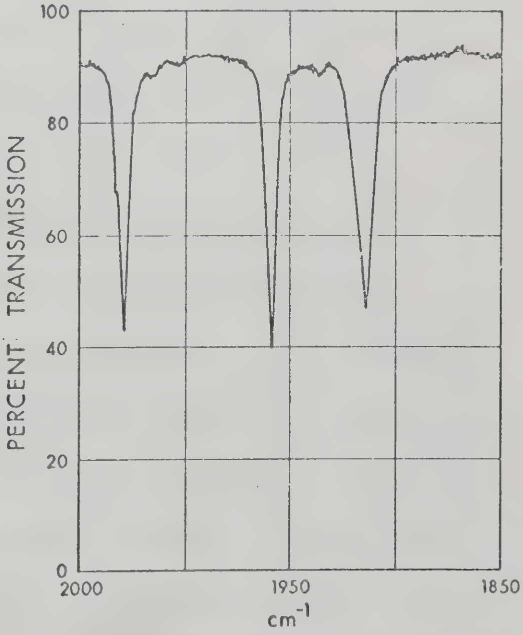
$C_6F_5Mn(CO)_3\,[P(OC_2H_5)_3]_2$

FIGURE 13



$C_6F_5Mn(CO)_3\,[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$

FIGURE 14



$C_6F_5Mn(CO)_3(CH_3SCH_2CH_2SCH_3)$

FIGURE 15

atoms in the bistriethylphosphite complex (see nmr results below).

On the other hand, the bis(1,2 diphenylphosphino)-ethane and 2,5-dithiahexane derivatives must, by the structure of these ligands, be substituted at adjacent sites. Consistent with an all *cis* arrangement for the carbonyl groups (VII), these derivatives show three carbonyl stretching bands of approximately equal intensity in their infrared spectra. In contrast, the appearance of only two bands in the infrared spectrum of $C_6H_5Mn(CO)_3$-$[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$ resulted in the proposal (86) that two of the carbonyl groups are *trans* to each other with all carbonyl groups *cis* to the phenyl ring (analogous to VI).

^{19}F NMR Spectra. Analysis of the ^{19}F nmr spectra was effected using well established methods (51,53) and the resulting parameters are listed in Table VIII. As a typical example, the spectrum of $C_6F_5Mn(CO)_5$ in acetone solution is shown in Figure 16. Acetone was used as solvent rather than the more common benzene; this modification was necessary as not all of the compounds prepared were sufficiently soluble in the latter solvent. Such a change in solvent fortunately did not greatly alter the nmr parameters as may be seen from the results for $C_6F_5Mn(CO)_5$ and $C_6F_5Mn(CO)_4Sb(C_6H_5)_3$ (Table III). Acetone did, however, reduce the stability of the complexes, particularly those of pyridine and 2,5-dithiahexane. The

TABLE VIII

^{19}F NMR Spectral Data[a]

Compound	ϕ_o[b]	ϕ_p[b]	ϕ_m[b]	$\pm J_{24}$	$\mp J_{34}$	$\mp J_{23}$	$\pm J_{25}$	$\mp J_{35}$	$\mp J_{26}$	J_{P3}	J_{P4}
$C_6F_5Mn(CO)_5$	102.5	158.7	162.4	0	19.1	28.1	9.2	2.8	8.3		
$C_6F_5Mn(CO)_5$[d]	103.5[e]	157.5[e]	161.3[e]	0	19.5[f]						
$C_6F_5Mn(CO)_4P(n\text{-}C_4H_9)_3$	100.7	161.5	162.6	0	19.4						0.8
$C_6F_5Mn(CO)_4P(C_6H_5)_3$	99.3	161.5	162.6	0	19.3	29.3	9.4	3.6	8.7	0.9	1.8
$C_6F_5Mn(CO)_4As(C_6H_5)_3$	99.0	160.2	162.4	0	19.4	29.4	9.6	3.4	8.5		
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$	97.4	160.0	162.1	0	19.3	29.5	9.5	3.2	8.5		
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$[d]	98.1	160.0	162.3	0							
$C_6F_5Mn(CO)_4P(OC_6H_5)_3$	100.1	160.0	162.5	0	19.5	29.3	9.5	3.4	8.4	1.4	2.4
$C_6F_5Mn(CO)_4NC_5H_5$	106.5	160.2	162.9	0	19.2	29.6	10.2	3.7	7.6		
$C_6F_5Mn(CO)_3[P(n\text{-}C_4H_9)_3]_2$	97.5	162.6	163.0	0							
$C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$	97.5	162.9	164.6	0	19.3						2.5
$C_6F_5Mn(CO)_3[(C_6H_5)_2PCH_2CH_2\text{-}P(C_6H_5)_2]$	95.6	162.3	164.0	0	19.5						1.1
$C_6F_5Mn(CO)_3[CH_3SCH_2CH_2SCH_3]$	105.3	161.3	164.1	0	19.4	30.5	10.5	4.5	7.1		

---

[a] Obtained from approximately 10 mole % solutions in acetone unless otherwise stated. Nomenclature of reference 1 is used.

TABLE III (continued)

[b] Relative to $CFCl_3$, reference C_6F_6 (chemical shift = 163.0 ppm).

[c] Value of zero indicates $J_{24} \leq 0.7$ c.p.s.

[d] Obtained from approximately 5 mole % solutions in benzene.

[e] Lit: $\phi_o = 104.3$, $\phi_p = 157.5$, $\phi_m = 161.2$ (79,90); $\phi_o = 102.4$, $\phi_p = 155.7$, $\phi_m = 159.6$ (80), these values are corrected by addition of 76.5 ppm to the reported values in order to convert from the reference CF_3COOH to $CFCl_3$ (G.V.D. Tiers and G. Filipovich, J. Phys. Chem., 63, 761 (1959)).

[f] Lit: $J_{34} = 26(\pm 2)$ c.p.s. (80).

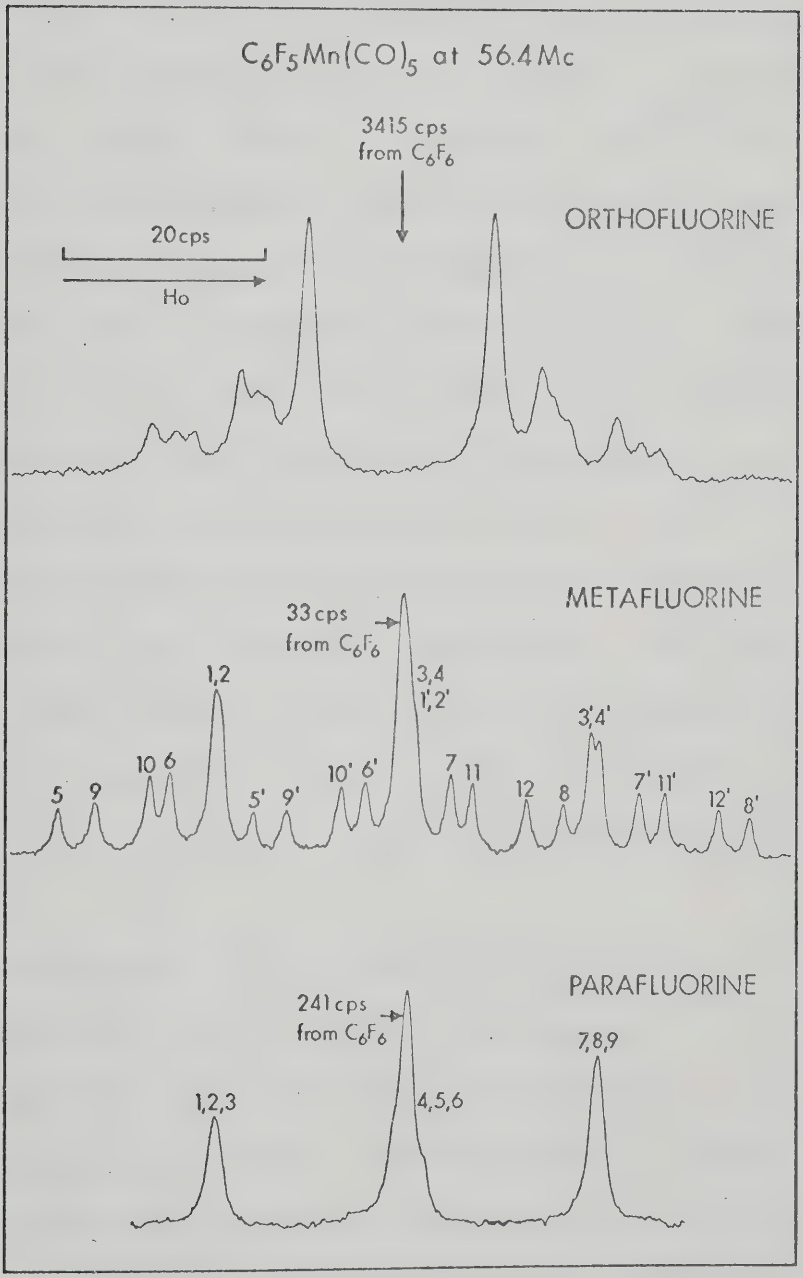


FIGURE 16. The ^{19}F NMR Spectrum of $C_6F_5Mn(CO)_5$ in acetone solution.

problems of insufficient solubility and decomposition meant that some coupling constants could not be evaluated.

Examination of the nmr parameters was expected to show a linear relationship between the coupling constant, J_{24}, and the p-fluorine chemical shift, ϕ_p, as has been found for a large number of compounds (51,52,53). A measure of the changes in π-electron density could then be qualitatively determined. It might be considered that a more quantitative approach could be taken by determining the parameters σ_I (87) and σ_{R° (88). This assumes that the equations which have been set up relating nmr results with these parameters (see equations 1 and 2, Table VI, reference 51) may be extrapolated to the compounds reported here. The equations were actually derived for only eight "common" organic substituents. Nevertheless an attempt was made to determine values for σ_I and σ_{R° but the results, particularly for σ_I, were at variance with those which were hopefully expected.

For example, in the case of $C_6F_5Mn(CO)_5$, calculated Taft parameters are $\sigma_I = +0.33$ and $\sigma_{R^\circ} = -0.21$; the former value would imply an inductive withdrawal by the pentacarbonylmanganese group. Thus electronic interactions with the pentafluorophenyl group cannot be reliably determined by this method although reasonable results have been obtained for monofluorophenyl derivatives (78). Further investigation will be required to discover why extrapolation is not valid in the former case.

The qualitative relation between J_{24} or ϕ_p and π-bonding to the pentafluorophenyl ring seems to remain tenable and J_{24} values near zero in all cases imply that the manganese carbonyl substituents are weak π-donors relative to hydrogen [for C_6F_5H, $J_{24} = 1.3$, $\phi_p = 154.3$ (51,53)]. Substitution of carbon monoxide by another ligand certainly changes the π-electron distribution as evidenced by a shift in the stretching frequencies of the remaining carbonyl groups. If a poorer π-acceptor such as triphenylphosphine replaces carbon monoxide then an increased donation of metal electron density into the π^* orbitals of the remaining carbonyl groups may be expected. This implies a general decrease in the CO stretching frequencies as is observed. Some increased donation to the π-system of the pentafluorophenyl group might also be anticipated and this should be evident from the ^{19}F nmr results. Although changes in ϕ_p are rather small there is confirmation of the π-bonding proposal for the values of ϕ_p seem to increase with increasing replacement of carbonyl groups. The lack of influence on the aromatic system by such substitution can be attributed either to poor overlap of the aromatic π-system and the π-system on the metal or to a more facile change of π-electron density in the carbonyl system compared to the pentafluorophenyl ring.

Of particular interest is the low shielding of the o-fluorine atoms in these manganese compounds, which in fact exhibit the lowest ϕ_o values of any reported penta-

fluorophenyl derivatives. A large paramagnetic contribution to the screening is to be expected by analogy with the ^{19}F nmr results for α fluorine atoms present in perfluoroalkyl-metal complexes (89). However, in contrast to these perfluoroalkyl complexes, pentafluorophenyl derivatives show a higher sensitivity to the electronegativity of the atom to which the perfluoro-organic group is attached (51,53). Thus the shift to low field of o-fluorine atoms may be attributed to the major effects of low-lying excited energy levels mixing with the ground state of the molecule to cause paramagnetic screening (90), and of the relatively electropositive nature of the manganese atom.

In a few compounds it was possible to measure the coupling of phosphorus to p-fluorine. Thus the p-fluorine nmr spectra were observed as triplets of doublets for monosubstituted compounds or as triplets of triplets for disubstituted derivatives. A triplet of triplets would also be expected if J_{24} were significant and the phosphorus coupling were negligible. A value of J_{24} close to zero is, however, expected in view of the ϕ_p values and the quite firmly established $J_{24} - \phi_p$ relationship. We believe therefore, that the assignment of the smaller coupling to phosphorus is correct and this is consistent with the phosphorus coupling observed in all phosphine and phosphite derivatives which allowed measurement. Taking this assignment as correct, it follows that both phosphorus atoms in the bistriethylphosphite and bisdiphenylphosphinoethane derivatives are

in magnetically equivalent and most probably symmetrically equivalent, environments. This is, of course, consistent with the structural assignments made on the basis of the infrared spectra.

EXPERIMENTAL

Reactions were carried out and solvents dried as given in Chapter II. The ligands used in this study came from commercial sources and were reacted without further purification.

Analyses were obtained as before with the results given in Table IX. Infrared spectra were measured using a Perkin-Elmer Model 337 (grating) spectrometer with a Texas Instruments Servo-Riter recorder. Bands of gaseous CO and DBr at 2147.1 cm^{-1} and 1804.9 cm^{-1} respectively were used as references for the accurate determination of other band positions. Mass spectra and ^{19}F nmr spectra were recorded as before.

Preparation of $C_6F_5Mn(CO)_5$. Pentafluorobenzene (1.41 ml, 12.8 mmol) was dissolved in diethyl ether (25 ml), the solution cooled to -70°, and a 1.55 M solution of n-butyllithium (8.22 ml, 12.8 mmol) in hexane added slowly. The mixture was allowed to warm to -10° and kept at that temperature for 1 h. The resulting solution was cooled again to -70° and a suspension of manganese pentacarbonyl bromide (3.50 g, 12.8 mmol) in 10 ml of ether was added. The mixture was allowed to attain room temperature slowly and was stirred for 14 h.

After evaporating to dryness, the residue was chromatographed in benzene solution on alumina. The required product is first to pass through the column but does contain a little $Mn_2(CO)_{10}$. The latter is easily removed by fractional sub-

limation to yield pure pentafluorophenylmanganese pentacarbonyl (2.98 g, 8.25 mmol, 65%).

Preparation of Tri-n-butylphosphine complexes. To a solution of tri-n-butylphosphine (0.84 g, 4.2 mmol) in 20 ml of xylene was added pentafluorophenylmanganese pentacarbonyl (1.5 g, 4.1 mmol). The mixture was heated at 135° for 3 days, cooled, and the solvent removed under reduced pressure. The resulting solid was subjected to sublimation under high vacuum at 60° to give colorless oily crystals. On resublimation, the volatile product (0.26 g, 0.48 mmol) remained slightly impure but was confirmed to be $C_6F_5Mn(CO)_4P(\underline{n}-C_4H_9)_3$ by an exact mass measurement of its parent ion in the mass spectrum: calculated mass = 536.0947, measured mass = 536.0948. The nonvolatile product was recrystallized twice from hexane to yield pale yellow crystals of $C_6F_5Mn(CO)_3[P(n-C_4H_9)_3]_2$ (1.1 g, 1.6 mmol).

Preparation of $C_6F_5Mn(CO)_4P(C_6H_5)_3$. Pentafluorophenylmanganese pentacarbonyl (1.0 g, 2.8 mmol) and triphenylphosphine (0.74 g, 2.8 mmol) were added to 30 ml of toluene and the mixture was heated at 90° for 3 days. After removal of solvent under reduced pressure, the residue was taken up in the minimum of hexane, filtered, and cooled to yield pale yellow crystals. These were recrystallized once from hexane to give the pure product (1.1 g, 1.8 mmol).

The same procedure was used for the preparation of the compounds $C_6F_5Mn(CO)_4As(C_6H_5)_3$, $C_6F_5Mn(CO)_4Sb(C_6H_5)_3$

and $C_6F_5Mn(CO)_4P(OC_6H_5)_3$; for the latter derivative a twofold excess of ligand was used.

Preparation of $C_6F_5Mn(CO)_4NC_5H_5$. Pentafluorophenylmanganese pentacarbonyl (6.0 g, 17 mmol) was dissolved in 250 ml of dichloromethane and pyridine (1.5 ml, 1.3 g, 16 mmol) was added. This solution was irradiated for 40 min. at 10° by a 450 watt Hanovia 679A lamp. Dichloromethane and excess pyridine were removed at reduced pressure, the remaining solid taken up in chloroform, and the solution filtered. Evaporation of chloroform yielded a yellow solid which was sublimed at room temperature for 3 days under high vacuum to remove unreacted pentacarbonyl (0.9 g, 2.5 mmol). The unsublimed material was recrystallized twice from hexane to yield the pure product (0.58 g, 1.5 mmol) as light yellow crystals.

Preparation of $C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$. Technical grade triethylphosphite (1.2 g, 5.8 mmol) and pentafluorophenylmanganese pentacarbonyl (1.0 g, 2.8 mmol) were dissolved in 30 ml of methylcyclohexane. The mixture was heated for 12 h at 80° and, after cooling, solvent was removed under reduced pressure. The resulting white solid was recrystallized twice from hexane to yield fine white needles (1.43 g, 2.2 mmol).

Preparation of $C_6F_5Mn(CO)_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$. Bis-(1,2 diphenylphosphino) ethane (1.1 g, 2.8 mmol) was added

to a solution of pentafluorophenylmanganese pentacarbonyl (1.0 g, 2.8 mmol). After heating for 24 h at 90°, solvent was removed under reduced pressure. Recrystallization from benzene yielded the pure product (1.45 g, 2.03 mmol).

Preparation of $C_6F_5Mn(CO)_3(CH_3SCH_2CH_2SCH_3)$. Pentafluorophenylmanganese pentacarbonyl (1.5 g, 4.1 mmol) and 2,5-dithiahexane (0.65 g, 5.3 mmol) were heated together in 30 ml of methylcyclohexane for 3 days at 90°. The mixture was cooled to 0° and the resulting solid collected. Excess pentafluorophenylmanganese pentacarbonyl (0.15 g, 0.4 mmol) was removed by sublimation under high vacuum at 50° and the remaining material extracted with dichloromethane. After addition of pentane and cooling to -15°, the pure product (0.9 g, 2.1 mmol) was obtained.

TABLE IX

Analytical Data

	Calculated				Found			
	C	H	F	P	C	H	F	P
$C_6F_5Mn(CO)_5$	36.50	0.00			36.66	0.00		
$C_6F_5Mn(CO)_4P(C_6H_5)_3$	56.40	2.54	15.93	5.19	56.06	2.42	15.59	5.04
$C_6F_5Mn(CO)_4As(C_6H_5)_3$	52.53	2.36	14.84		52.10	2.54	14.42	
$C_6F_5Mn(CO)_4Sb(C_6H_5)_3$	48.95	2.20	13.82		48.68	2.04	12.45	
$C_6F_5Mn(CO)_4P(OC_6H_5)_3$	52.19	2.35	14.74	4.81	52.71	2.52	14.65	4.71
$C_6F_5Mn(CO)_4NC_5H_5$	43.61	1.22	22.99		43.95	1.18	22.19	
$C_6F_5Mn(CO)_3[P(n\text{-}C_4H_9)_3]_2$	55.77	7.66	13.37		55.85	7.36	13.14	
$C_6F_5Mn(CO)_3[P(OC_2H_5)_3]_2$	39.51	4.74			39.68	4.87		
$C_6F_5Mn(CO)_3](C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$	59.67	3.43			59.64	3.45		
$C_6F_5Mn(CO)_3(CH_3SCH_2CH_2SCH_3)$	36.46	2.35	22.18		37.05	2.29	22.07	

CHAPTER IV

A REVIEW OF CYCLOPENTADIENYL DERIVATIVES OF RHODIUM AND IRIDIUM

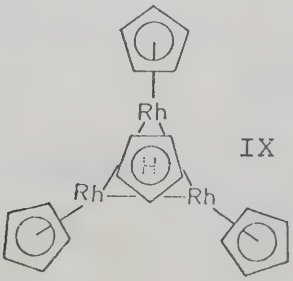
A. Cyclopentadiene Derivatives

After the preparation of ferrocene there was much interest in possible analogues of other metals. Thus in 1953 the isoelectronic species Cp_2Rh^+ (VIII) and Cp_2Ir^+ (Cp refers to the pentahaptocyclopentadienyl group (91) throughout this Chapter) were produced (92) by the reaction of rhodium or iridium triacetylacetonates with a cyclopentadienyl Grignard reagent and subsequent precipitation as the I_3^- salts [IV.1].

$$\begin{matrix} Rh(CH_3COCHCOCH_3)_3 \\ + C_5H_5MgBr \end{matrix} \longrightarrow \xrightarrow{I_3^-} [Cp_2Rh]^+ I_3^- \qquad [IV.1]$$

Almost identical reactions have since been found using the chlorides instead of the acetylacetonates, and the products were isolated as the Br_3^- and PF_6^- salts (93,94). Other rhodocinium (i.e. Cp_2Rh^+) salts can be made by replacement of one anion by another large anion (92).

When $RhCl_3$ is used in reaction [IV.1] a most unusual by-product, Cp_4Rh_3H, was obtained in 3% yield (95,96). The structure has been determined as IX by X-ray diffraction



IX

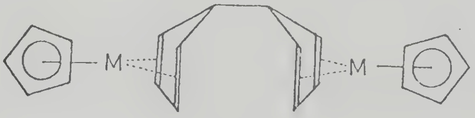
(95,97), and the presence of the unique hydrogen atom confirmed by nmr and mass spectrometry (95,96).

The first reported preparation of rhodocene, Cp_2Rh, employed the very novel procedure of bombarding ruthenocene with neutrons [IV.2] (98).

$$Cp_2{}^{104}Ru \xrightarrow{n,\gamma} Cp_2{}^{105}Ru \xrightarrow{\beta^-,\gamma} Cp_2{}^{105}Rh \xrightarrow{\beta^-} Cp_2{}^{104}Rh$$

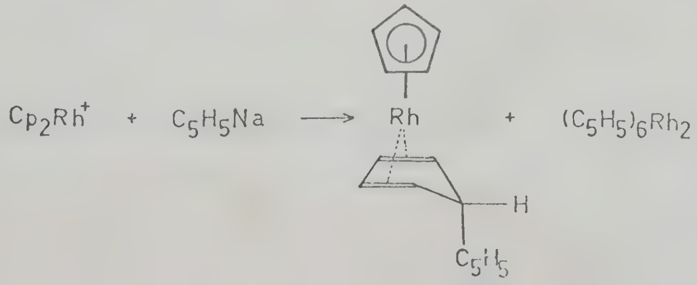
[IV.2]

The product, however, was not well characterised and alternative proposals as to the composition of the product have been made (99). Subsequently the species Cp_2M (M = Rh and Ir throughout this Chapter) were prepared by the reduction of $(Cp_2M)^+(PF_6)^-$ by molten sodium (94) with immediate sublimation of the product to a finger cooled by liquid nitrogen. At room temperature dimerisation takes place to give X.



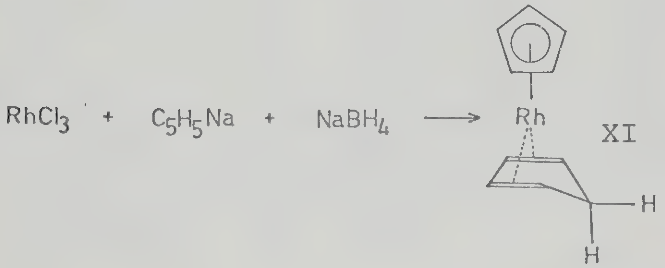
X

The rhodocinium ion (VIII) has been reduced by sodium cyclopentadienide and by phenyllithium (93) to afford a product with the cyclopentadienyl or phenyl group in the *exo* position [IV.3] and also in the former case a compound,



[IV.3]

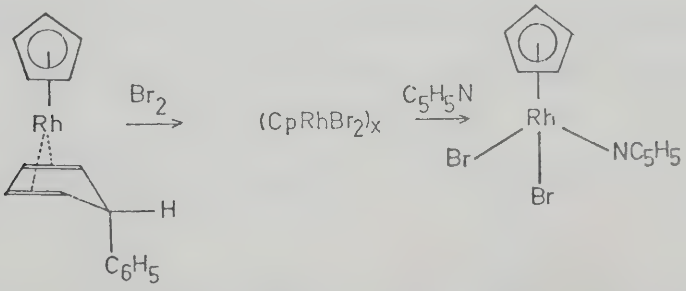
$(C_5H_5)_6Rh_2$, whose structure remains unknown. Essentially, the same reaction takes place on reaction of sodium borohydride and sodium cyclopentadienide with rhodium trichloride but the intermediate rhodocinium salt is, of course, not isolated [IV.4] (100). The compound (XI)



XI

[IV.4]

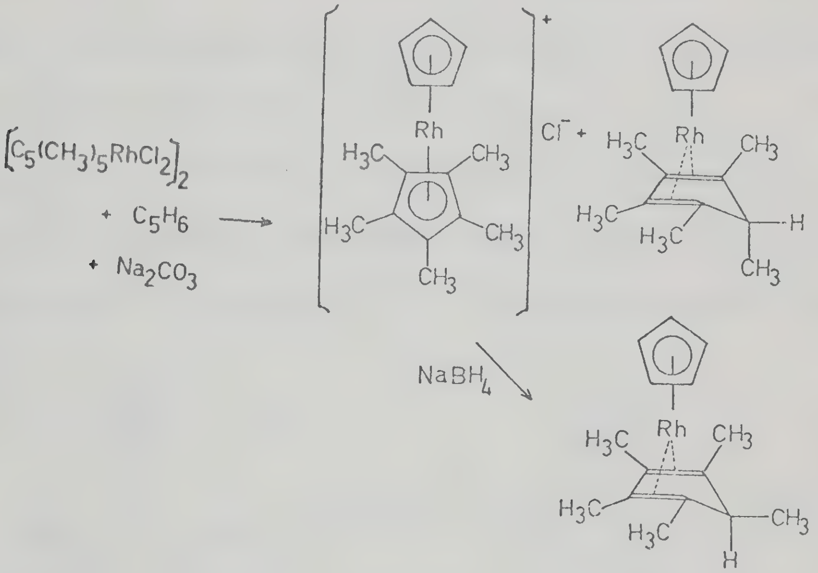
and its iridium analogue have also been prepared by reaction of the anhydrous trichloride, sodium cyclopentadienide and cyclopentadiene (101). Acidified hydrogen peroxide oxidises $CpMC_5H_6$ and related compounds, such as $CpRh(C_5H_5C_6H_5)$, to remove a hydride ion with consequent formation of $(Cp_2M)^+$ or its derivatives. These were isolated as tetraphenylboron salts (101). Reaction of $CpRh(C_5H_5C_6H_5)$ with bromine appears to give the polymer $(CpRhBr_2)_x$ [IV.5], which



[IV.5]

may be broken down by pyridine (93).

Almost the reverse of reaction (IV.5] has been shown in the reduction of pentahaptopentamethylcyclopentadienylrhodium dichloride dimer with cyclopentadiene and sodium carbonate in ethanol [IV.6] (102). One product contains the *endo*-H isomer of pentamethylcyclopentadiene. Reduction


$[C_5(CH_3)_5RhCl_2]_2$
+ C_5H_6
+ Na_2CO_3
Rh
H_3C
CH_3
H_3C
CH_3
CH_3
+
Cl^- +
H_3C
Rh
CH_3
H_3C
H_3C
H
CH_3
$NaBH_4$
H_3C
Rh
CH_3
H_3C
H_3C
CH_3
H

[IV.6]

of the other product, which is a mixed rhodocinium salt, affords the corresponding *exo*-H isomer.

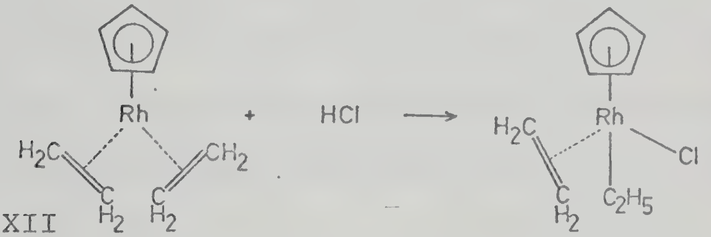
B. Other Olefin Derivatives

The moiety CpRh has been shown to accept two olefinic groups as ligands (e.g. compounds X and XI); thus the prototype of this kind of compound is $CpRh(C_2H_4)_2$ (XII), prepared by reaction [IV.7] (103). By a similar method

$$[(C_2H_4)_2RhCl]_2 + C_5H_5Na \longrightarrow \underset{\text{XII}}{CpRh(C_2H_4)_2} \qquad [IV.7]$$

$CpRh(H_2C = CHCH_2CH_2CH{=}CH_2)$ has been formed (104) and the pentamethylcyclopentadienylbisethylene compounds of both rhodium and iridium have also been reported recently (105).

Nmr studies indicate that the ethylene ligands of XII rotate about their μ bonds but do not exchange (104). The rotation is slower in $C_5(CH_3)_5Ir(C_2H_4)_2$ than in the rhodium analogue (105) showing the typically better π-bonding of third-row compared to second-row transition metals. Replacement of ethylene in XII is possible by Lewis acids; thus SO_2 yields $CpRh(SO_2)(C_2H_4)$ (106) but a base such as triphenylphosphine will not react. Treatment of XII by hydrogen chloride at -60° gives an ethylchloro derivative [IV.8] (106), identified by nmr,

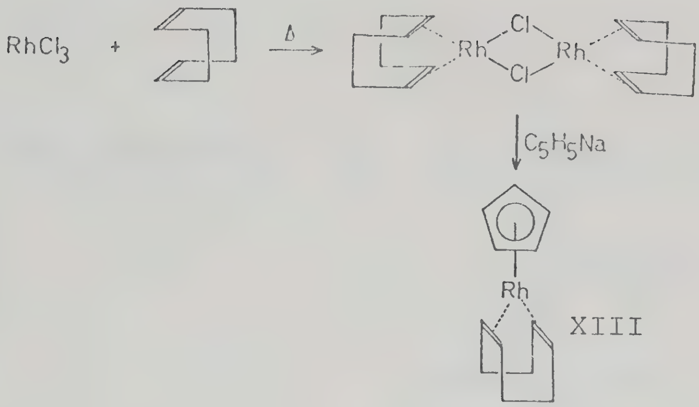


[IV.8]

but this product decomposes at -20°.

In addition to those involving cyclopentadiene, diene complexes are known which contain cyclooctadiene (107,108,109,110), norbornadiene (III), duroquinone (112) or 2,6 ditert-butylbenzoquinone (1,4) (113,114,115). These derivatives are prepared by reaction of the diene with MCl_3 and subsequent reaction of the product with sodium cyclopentadienide, e.g. [IV.9]. Compounds XII and XIII have been studied by mass spectrometry (109).

With mercuric halides the cyclooctadiene (XIII) and



XIII

[IV.9]

norbornadiene derivatives form adducts such as $CpRhC_7H_8 \cdot HgCl_2$ (111) and $CpIrC_8H_{12} \cdot HgBr_2$ (110).

Not only has 2,6 ditert-butylbenzoquinone (1,4) been used to prepare $CpRh\ [2,6(C_4H_9)_2C_6H_2O_2]$ (XIV), but also the analogous indenyl complex from potassium indenide (113). The compound (XIV) has been subjected to an X-ray structural determination (114) and to polarographic studies (115).

Allyl derivatives of cyclopentadienylrhodium are also known; the first prepared was $CpRh(C_3H_5)_2$ (XV) [IV.10] (116)

$$[(C_3H_5)_2RhCl]_2 + TlC_5H_5 \longrightarrow \underset{\text{XV}}{CpRh(C_3H_5)_2} + TlCl \qquad [IV.10]$$

which presumably contains one π and one σ bonded allyl group. Hydrogen chloride reacts with XV according to equation [IV.11]. A π crotyl complex analogous to XVI has also been made by a

$$\begin{tikzcd} CpRh(C_3H_5)_2 + HCl \arrow[r] & CpRh(C_3H_5)Cl \ \text{XVI} \arrow[d] \\ & (CpRhCl_2)_2 \end{tikzcd} \qquad [IV.11]$$

rather novel route [IV.12].

$$\begin{tikzcd} \mathrm{RhCl_3 + CH_2{=}CH{-}CH{=}CH_2} \arrow[r] & \mathrm{(C_4H_7)_2Rh_2Cl_4(C_4H_6)} \arrow[d, "\mathrm{TlC_5H_5}"] \\ & \mathrm{CpRh(C_4H_7)Cl} \end{tikzcd} \qquad [IV.12]$$

C. Carbonyl Compounds

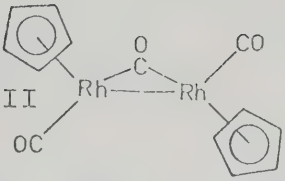
Cyclopentadienyldicarbonylrhodium (XVII) is prepared by the reaction of dicarbonylrhodium chloride dimer with excess sodium cyclopentadienide [IV.13] (118,119). The analogous

$$[(CO)_2RhCl]_2 + C_5H_5Na \longrightarrow \underset{\text{XVII}}{CpRh(CO)_2} + NaCl \qquad [IV.13]$$

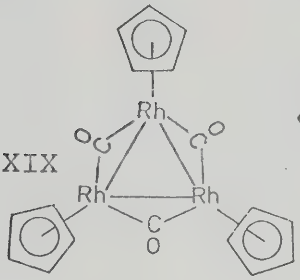
iridium compound was formed in similar fashion using $Ir(CO)_3Cl$ (120). The pentamethylcyclopentadienyliridium derivative, $C_5(CH_3)_5Ir(CO)_2$, has been formed from $[C_5(CH_3)_5IrCl_2]_2$ (see equation IV.26) in two ways: (i) reduction with sodium carbonate under carbon monoxide pressure (ii) reflux with $Fe_3(CO)_{12}$ in benzene (121). The nmr spectra of the indenyl derivatives $C_9H_7M(CO)_2$ (122) have been reported, although the preparations of these compounds are not given.

On irradiation in pentane or hexane, XVII loses carbon monoxide to produce the metal clusters $Cp_2Rh_2(CO)_3$ (XVIII) and $(CpRhCO)_3$ (123,124,125). Examination of these compounds by X-ray spectroscopy has revealed their structures and show that the latter compound exists in two distinct isomers, XIX and XX. The structures are all of great

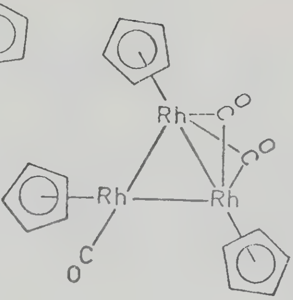
XVIII



XIX



XX



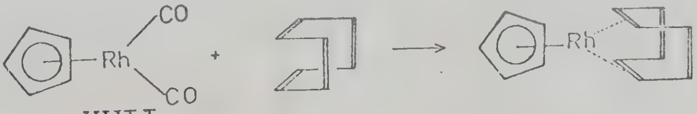
interest since XVIII is the first binuclear carbonyl complex with a single bridging CO group (124). Also XIX and XX represent the first case where X-ray spectroscopy has shown the difference between possible bridged and non-bridged forms of a carbonyl compound (123,125).

Mixed metal cluster compounds have been formed by reaction of XVII with $Fe_2(CO)_9$ [IV.14] (126) but as yet

$$CpRh(CO)_2 + Fe_2(CO)_9 \longrightarrow CpRhFe_2(CO)_9 + CpRhFe_3(CO)_{11}$$
$$Cp_2Rh_2Fe(CO)_6 + Cp_2Rh_2Fe_2(CO)_8 \qquad [IV.14]$$

no structural determinations have been made on these derivatives.

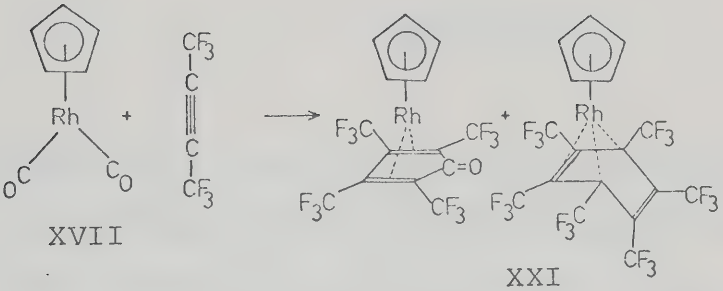
Carbon monoxide is eliminated from XVII by a variety of ligands. Refluxing with cyclooctatetraene causes complete elimination [IV.15] (127). Hexafluorobut-2-yne



XVII

[IV.15]

affords two major products [IV.16] (128). Compound XXI has



XVII XXI [IV.16]

found by X-ray studies (129) to have a benzene ring with a bent structure presumably owing to localised bonding. It must be remembered, however, that it is sterically impossible for hexa(trifluoromethyl)benzene to be planar (130).

Phosphines, phosphites and isocyanides also displace carbon monoxide from XVII (131). Only monosubstituted derivatives may be obtained with phosphines but both mono and disubstitution can take place with phosphites and isocyanides [IV.17]. A bis-substituted phosphorus trifluoride

$$\begin{tikzcd}
\underset{\text{XVII}}{CpRh(CO)_2} + P(OCH_3)_3 \arrow[r] & CpRh(CO)P(OCH_3)_3 \arrow[d, "P(OCH_3)_3"] \\
& CpRh[P(OCH_3)_3]_2
\end{tikzcd} \qquad [IV.17]$$

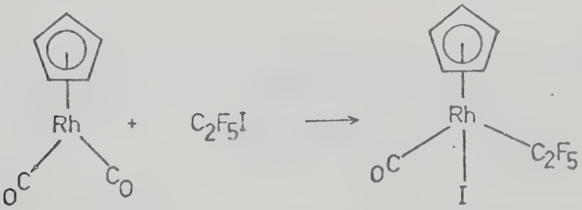
complex has also been made by a different route [IV.18] (132).

$$\begin{tikzcd}(C_8H_{14}RhCl)_2 + PF_3 \arrow[r] & [(PF_3)_2RhCl]_2 \arrow[d, "C_5H_5Tl"] \\ & CpRh(PF_3)_2\end{tikzcd} \qquad [IV.18]$$

Triphenylphosphine is reported to react with $CpIr(CO)_2$ to yield $CpIr(CO)P(C_6H_5)_3$ (131) but this product was poorly characterised. Azobenzene causes loss of carbon monoxide from XVII (133), however, it remains difficult to formulate a structure for the product [IV.19].

$$\underset{\text{XVII}}{CpRh(CO)_2} + C_6H_5NNC_6H_5 \longrightarrow CpRh(HNC_6H_4NC_6H_5) \qquad [IV.19]$$

Oxidation of XVII has been noted with iodine (134) and the pseudo-halogens CF_3I, C_2F_5I and C_3F_7I [IV.20] (135).



XVII XXII

[IV.20]

An asymmetric centre was confirmed to be present at rhodium in XXII by an ^{19}F nmr study (135) and subsequently a crystal structure determination showed the compound to exist as a racemate (136).

Possibly the only reaction of XVII in which carbon

monoxide is not eliminated is the formation of an adduct with the Lewis acids $HgCl_2$ and $HgBr_2$ [IV.21] (110).

$$CpRh(CO)_2 + HgCl_2 \longrightarrow CpRh(CO)_2 \cdot HgCl_2 \qquad [IV.21]$$

D. Halide Derivatives

Some halogen compounds have been mentioned above but a few more remain for discussion. A most unusual preparation of $(CpRhI_2)_x$ has been reported (137) from bis(cycloocta-1,5-diene)-μ,μ'-dichlorodirhodium [IV.22] but attempts to repeat

$$(C_8H_{12}RhCl)_2 + I_2 \xrightarrow{0°\text{, ether}} (CpRhI_2)_x \qquad [IV.22]$$

this work by the original authors and by others (121) have failed. Thus this reaction must be viewed with reserve. In the same suspect work some derivatives of $(CpRhI_2)_x$ were reported [IV.23]. A dimethylsulfur derivative similar

$$(CpRhI_2)_x + (C_6H_5)_3P \longrightarrow CpRhI_2P(C_6H_5)_3 \xrightarrow{CH_3MgI} CpRh(CH_3)_2P(C_6H_5)_3 \qquad [IV.23]$$

to XXIII has also been prepared [IV.24] (138).

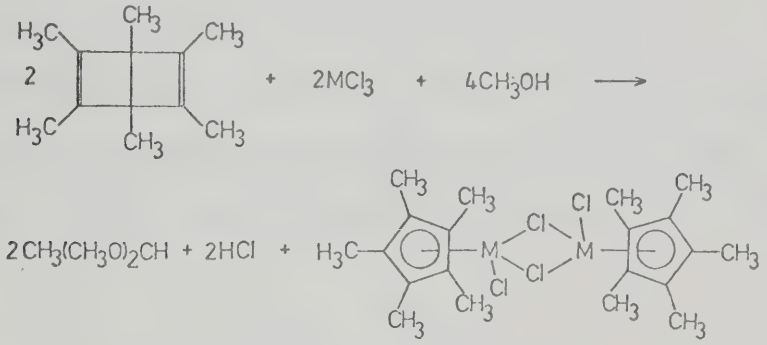
$$Rh_2I_2(CH_3)_4[S(CH_3)_2]_3 + C_5H_5Na \longrightarrow CpRh(CH_3)_2S(CH_3)_2 \qquad [IV.24]$$

The polymeric halide $(CpRhBr_2)_x$ [IV.5] has been treated with a dithiolate salt to afford a monomeric derivative [IV.25] (139).

$$(CpRhBr_2)_x + Na_2C_2H_2S_2 \longrightarrow CpRhS_2C_2H_2 + NaBr \qquad [IV.25]$$

E. Pentamethylcyclopentadienyl Derivatives

Much work has recently been reported by Maitlis and coworkers (102,105,121,140,141) on pentahaptopentamethylcyclopentadienyl derivatives of rhodium and iridium, some of which has been mentioned above [IV.6]. The dimers $[C_5(CH_3)_5MCl_2]_2$ (XXIV) are prepared by the reaction of hexamethyl (Dewar) benzene with the metal trichlorides in methanol [IV.26] (140,141,142). The dimeric chlorides (XXIV) will undergo halogen exchange when treated in solution with sodium iodide and both chloride and iodide dimers can be broken down to monomers $C_5(CH_3)_5MX_2L$ with ligands L such as triphenylphosphine, pyridine or p-toluidine. The di-iodo triphenylphosphine monomer was further reacted with a methyl Grignard reagent to yield both dimethyl and methyliodo products [IV.27] (121).



XXIV

[IV.26]

$$C_5(CH_3)_5RhI_2L + CH_3MgI \longrightarrow \qquad [IV.27]$$

$$C_5(CH_3)_5RhI(CH_3)L + C_5(CH_3)_5Rh(CH_3)_2L$$

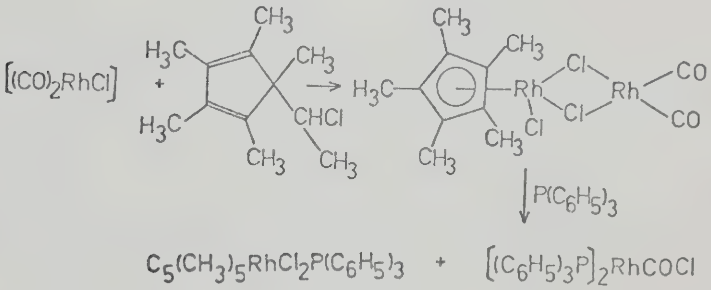
The compound XXIV has also led to an interesting series of reactions with 1,2bis(diphenylphosphino)ethane

(diphos), [IV.28] (121).

$$\begin{tikzcd}
\mathrm{XXIV} + \mathrm{diphos} \arrow[r] & {[C_5(CH_3)_5Cl_2Rh \leftarrow P(C_6H_5)_2CH_2-]_2} \arrow[d, "\mathrm{diphos}"] \\
{[C_5(CH_3)_5RhCl(\mathrm{diphos})]^+PF_6^-} & C_5(CH_3)_5Cl_2Rh(\mathrm{diphos}) \arrow[l, "NH_4^+PF_6^-"']
\end{tikzcd}$$

[IV.28]

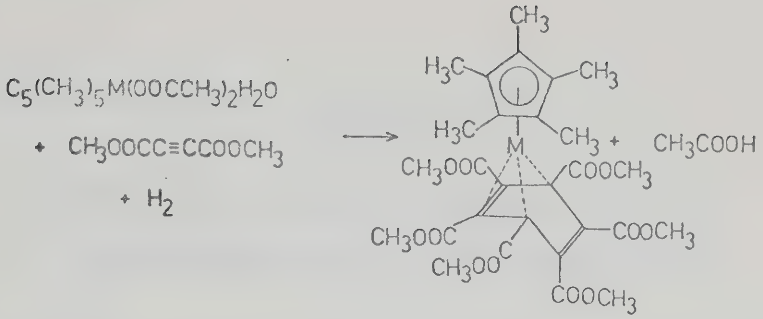
A mixed dimeric species is obtained by reaction of dicarbonylrhodium chloride dimer with 1-(1-chloroethyl)pentamethylcyclopentadiene in methanol [IV.29] (121) and this product can be broken down into monomers with the ligands


[(CO)2RhCl]
+
H3C
H3C
CH3
CH3
CHCl
CH3
CH3
H3C
CH3
CH3
Rh
Cl
Cl
Cl
Rh
CO
CO
CH3
CH3
P(C6H5)3
C5(CH3)5RhCl2P(C6H5)3
+
[(C6H5)3P]2RhCOCl

[IV.29]

triphenylphosphine and p-toluidine.

Some tetrahaptobenzene complexes of rhodium and iridium similar to XXI [IV.16] have been formed from the diacetate derivative of XXIV, dimethylacetylenedicarboxylate and hydrogen [IV.30] (105).


C5(CH3)5M(OOCCH3)2H2O
+ CH3OOCC≡CCOOCH3
+ H2
CH3
H3C
CH3
H3C
CH3 +
CH3COOH
M
CH3OOC
COOCH3
CH3OOC
COOCH3
CH3OOC
COOCH3

[IV.30]

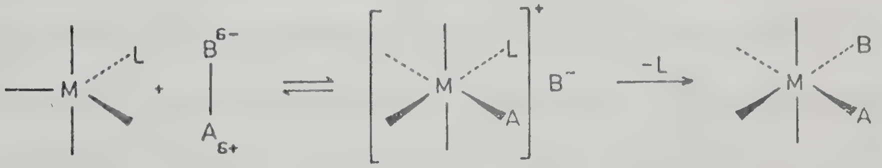
An nmr study of these derivatives shows fluxional behaviour of the benzene ligand: at 155° only one carboxylmethyl resonance is observed.

The work of Maitlis is perhaps the only detailed study of reactions of the cyclopentadienyl derivatives of rhodium and iridium and thus much work remains to be done in this field.

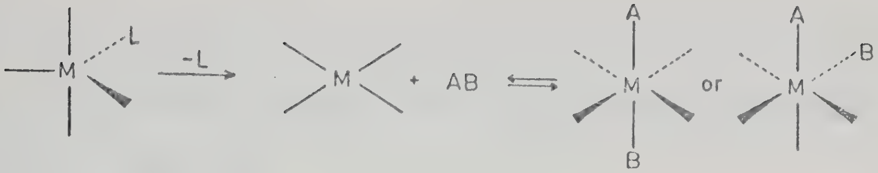
CHAPTER V

SOME GROUP IV METAL DERIVATIVES OF CYCLOPENTADIENYLDICARBONYLRHODIUM

The fact that cyclopentadienyldicarbonylrhodium undergoes reactions with iodine or perfluoroalkyl iodides accompanied by elimination of carbon monoxide has been mentioned in Chapter IV, [IV.20]. Such reactions fall into the general class of "oxidative addition" reactions (143) although in this case the more specific term "oxidative elimination" (144) seems preferable in order to express the loss of carbon monoxide. Oxidative addition reactions to d^8 complexes have been reviewed recently (143,145) and in the case of 18 electron, 5 coordinate systems are best generalized by equation [V.1]. An alternative pathway for such a reaction is through prior dissociation of a ligand to form a more reactive four-coordinate complex. Labilisation of a ligand is often brought about by heating or irradiating a five-coordinate complex, equation [V.2]. The importance of such reactions in homogeneous catalysis has



[V.1]

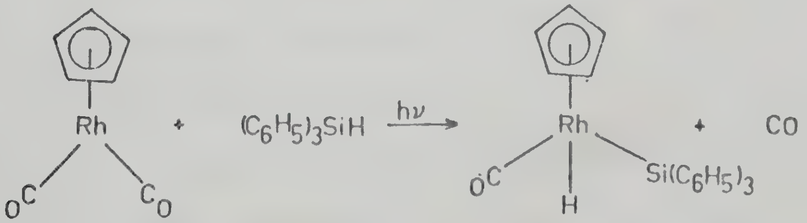

[V.2]

been stressed (145) and has encouraged the study contained in this and the following chapters.

Such oxidative methods could be expected to yield numerous Group IV metal derivatives of cyclopentadienyldicarbonylrhodium and this is verified by the findings reported here. The first germanium-rhodium bonds are described, although rhodium bonds to silicon (146,147,148) have been established recently and those to tin (149-154) have been known for some years.

RESULTS AND DISCUSSION

Irradiation of $CpRh(CO)_2$ in non-polar solvents has been reported to yield $Cp_2Rh_2(CO)_3$ (124) and $Cp_3Rh_3(CO)_3$ (123,125), probably via elimination of carbon monoxide and formation of the reactive intermediate "CpRhCO" (compare with equation [V.2]). The presence of a silane, however, appears largely to inhibit the formation of oligomers and gives the derivatives $CpCORh(H)SiR_3$ [V.3]


[V.3]

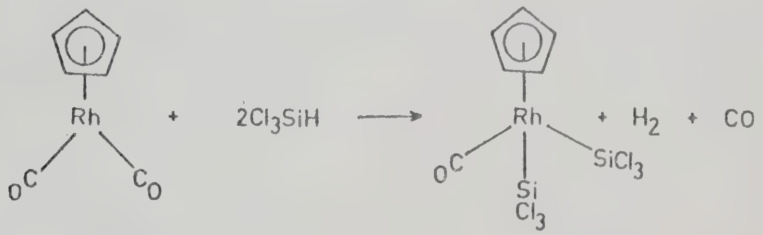
This is rationalised by preferential reaction of "CpRhCO" with the silane rather than with another molecule of rhodium compound.

Owing to difficulties in separation from starting materials, silyl hydride products could only be isolated using silanes of relatively high molecular weight (i.e. triphenyl and tribenzyl silanes). As solids these derivatives show signs of decomposition over a period of a few days at room temperature although they seem stable at -15°. In solution they are considerably less stable, particularly if polar solvents are used. Similar silyl hydrides have been reported from various silanes also by irradiation procedures (155,156,157).

An ^1H nmr spectrum of $CpCORh(H)Si(C_6H_5)_3$ was measured in carbon tetrachloride; this solvent was chosen in preference to chloroform, dichloromethane or acetone since the compound appears to decompose more rapidly in the latter solvents. Typical resonances were observed for phenyl and cyclopentadienyl protons; the most intense peak of the phenyl system was observed at τ 2.72 while the cyclopentadienyl resonance was observed as a triplet ($J = 0.5$ cps) at τ 4.77. The cyclopentadienyl protons might be expected to couple to ^{103}Rh (100% abundance with spin ½, see Chapters VI and VIII) and to the unique proton (158,159). Since a triplet is observed it must be concluded that the couplings of these two nuclei of spin ½ are equal in magnitude.

The hydrogen directly bonded to rhodium can be anticipated to couple to this metal (158,160) and thus a doublet (J = 31.8 cps) was observed at τ 21.1. The peaks were broad (width 3 cps) presumably because of coupling to the five cyclopentadienyl protons, mentioned above. It is of interest that this high field resonance is found at a chemical shift close to those observed for the unique protons in $CpMn(CO)_2(H)Si(C_6H_5)_3$ (τ 21.7) (157) and $CpRe(CO)_2(H)Si(C_6H_5)_3$ (τ 19.1) (157).

Trichlorosilane and methyldichlorosilane undergo very facile reactions with $CpRh(CO)_2$ to afford bis-silyl derivatives [IV.4], presumably via a silyl hydride species



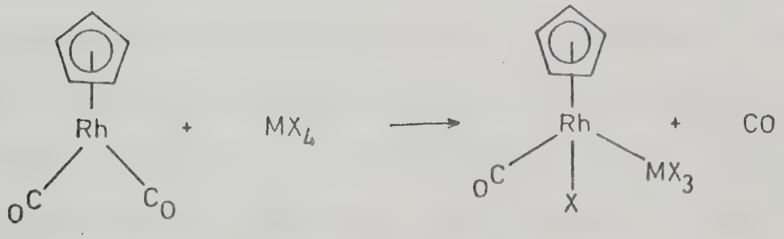
[IV.4]

as intermediate (155). The reactivity of $CpRh(CO)_2$ is interesting since $CpCo(CO)_2$ only reacts with trichlorosilane either with the assistance of ultraviolet light to give $CpCOCo(H)SiCl_3$ (155) or at 100° to give $CpCOCo(SiCl_3)_2$ (161).

The compound $CpCORh(SiCl_2CH_3)_2$ exhibited an ^1H nmr spectrum in $CDCl_3$ solution consistent with the proposed structure. One resonance which appeared as a sharp doublet at τ 4.33 can be assigned to the cyclopentadienyl

ring. A second doublet at τ 8.73 could be attributed to two methyl groups attached to silicon particularly as this resonance integrated with the cyclopentadienyl resonance in the ratio of 6:5. The doublet structures can be ascribed to coupling with rhodium and for both doublets J(Rh-H) = 0.8 cps. The compounds $CpCORh(SiCl_3)_2$ and $CpCOIRhSnI_3$ (see below) show resonances at τ 4.21 and τ4.00 respectively, owing to the cyclopentadienyl protons although the expected doublet structures could not be resolved.

Products of the type $CpCOXRhMX_3$ (M = Ge or Sn and X = Cl, Br or I) are formed under moderate conditions by the treatment of $CpRh(CO)_2$ with the tetrahalides of germanium and tin [V.5]. This is to be expected by analogy

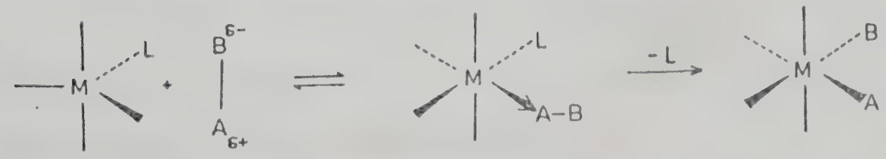


[IV.5]

with the reactions of $CpCo(CO)_2$ (162). However, although compounds of the type $CpCOCo(MX_3)_2$ could be isolated when an excess of halide and temperatures up to 110° were employed, only the compounds $CpCOXRhMX_3$ formed under similar reaction conditions. The inability to form $CpCORh(MX_3)_2$ is

rather surprising, not only because cobalt analogues can be prepared but because of the existence of the isoelectronic compounds $CpCORh(SiCl_3)_2$ and $C_6H_6CORu(GeCl_3)_2$ (163). It seems reasonable that this is a kinetic rather than thermodynamic effect, possibly attributable to a strong Rh-X bond which might inhibit the insertion of MX_2 (162).

In preparing the derivatives $CpCOXRhMX_3$, difficulty was experienced in two cases. Germanium tetraiodide gives a moderate yield of $CpCORhI_2$ which cannot easily be separated from the required product. The problem was overcome by using the method of halogen exchange on $CpCOClRhGeCl_3$. Stannic chloride in toluene or pentane reacts with $CpRh(CO)_2$ to afford a highly air-sensitive, orange-yellow powder which decomposes in air to give the required product. A similar intermediate is obtained with stannic bromide when pentane is used as solvent. Possibly these intermediates are adducts between the Lewis base, $CpRh(CO)_2$, and the Lewis acids, SnX_4, similar to adducts such as $CpRh(CO)_2 \cdot HgCl_2$ (110). Since these main group halides are acidic without loss of halide ions, perhaps for such cases [V.1] should be rewritten as [V.6]



[V.6]

Oligomeric compounds formed on reaction of $CpRh(CO)_2$ with stannous halides, but were difficult to characterise fully. Their high mass and relative insolubility makes them unsuitable for molecular weight determination, nuclear magnetic resonance or mass spectrometry. From the elemental analyses the derivatives were given the formulae $(CpCORhSnX_2 \cdot \frac{1}{3}\text{ Solvent})_x$ (see Table XI) however, the value of x is uncertain. A value of x equal to three seems most reasonable for in the compound $(CpCOCoSnCl_2 \cdot \frac{1}{3}C_6H_6)_x$, x was again considered to be three (164,165) and the compound $(CpCORhSnCl_2)_3$ could be expected to result from stannous chloride insertion into the known trimer $(CpRhCO)_3$ (123,125).

Infrared Spectra. Most compounds show one carbonyl stretching vibration (Table X) as expected for monocarbonyl molecules. However, the compounds $CpCORh(H)Si(CH_2C_6H_5)_3$, $CpCORh(SiCl_2CH_3)_2$ and $CpCOIRhSnI_2CH_3$ show extra bands in cyclohexane solution. Such effects, which may be attributed to the asymmetry of the substituents on rhodium have already been well documented and explained as due to conformers (44,162). The tribenzylsilane derivative is worthy of particular note since it is the asymmetry of the benzyl group rather than the asymmetry of the substituent arrangement around silicon or tin that likely causes the splitting of the infrared bands.

The proposed trimeric species each exhibit two

TABLE X

Physical Properties and Carbonyl Stretching Frequencies

Compound [a]	Color	% Yield	ν_{CO}, cm^{-1} [b]
$CpCORh(H)Si(C_6H_5)_3$ [c]	Off-white	11	2024[d]
$CpCORh(H)Si(CH_2C_6H_5)_3$ [e]	Off-white	10	2023m, 2020wsh, 2008s[d]
$CpCORh(SiCl_3)_2$ [f]	Colorless	61	2073[d]
$CpCORh(SiCl_2CH_3)_2$ [g]	Colorless	55	2050s, 2037m[d]
$CpCOClRhGeCl_3$	Orange	51	2098
$CpCOBrRhGeBr_3$	Red	82	2092
$CpCOIRhGeI_3$	Black	42	2080
$CpCOClRhSnCl_3$	Orange-red	35	2093
$CpCOBrRhSnBr_3$	Red	89	2087
$CpCOIRhSnI_3$	Black	71	2074
$CpCOIRhSnI_2CH_3$	Black	77	2060
			2067m, 2061s[d]
$[CpCORhSnCl_2 \cdot \frac{1}{3}C_2H_4Cl_2]_x$	Orange	58	2050s, 2034m
$[CpCORhSnCl_2 \cdot \frac{1}{3}C_6H_5CH_3]_x$	Orange	25	2052s, 2035m
$[CpCORhSnBr_2 \cdot \frac{1}{3}C_6H_5CH_3]_x$	Orange-red	14	2051s, 2033m
$[CpCORhSnCl_2]_n$	Orange	82	2058m, 2034s[h]

TABLE X (continued)

Footnotes to Table X.

[a] Decomposition temperatures around 200° and poorly defined (over 10 - 40° range) except as noted.

[b] Dichloromethane solution except as noted.

[c] 95 - 100° dec.

[d] Cyclohexane solution,

[e] 64 - 66° dec.

[f] 120 - 125° dec.

[g] 110 - 115° dec.

[h] Nujol mull.

carbonyl bands which are at virtually the same wave-numbers in each case, and are presumably also produced by a conformational effect. The exact nature of the conformers remains unknown as the geometries of the six-membered rings have not been determined. The polymeric species $(CpCORhSnCl_2)_n$ also exhibits two bands at similar wave-numbers but with reversed intensity pattern compared to the trimers. The splitting most probably has its origin in a conformational effect as in the other examples, although it may be due to crystal splitting.

Reactions of dichloromethane solutions of $(CpCORhSnCl_2.\frac{1}{3}C_2H_4Cl_2)_x$ or $(CpCORhSnCl_2.\frac{1}{3}C_6H_5CH_3)_x$ or a suspension of $(CpCORhSnCl_2)_n$ in dichloromethane with chlorine gas give solutions which show only one carbonyl stretching vibration at 2093 cm^{-1}. Thus the product in each case may be assumed to be $CpCOClRhSnCl_3$ (ν_{CO} = 2093 cm^{-1}) and this verifies the similarity of the starting materials.

EXPERIMENTAL SECTION

All reactions and crystallisations were carried out under a nitrogen atmosphere, mainly by the use of Schlenk-tube techniques. Solvents were dried as previously described. Published procedures were used for the preparation of GeI_4 (166), $SnBr_4$ (166), SnI_4 (166), CH_3SnI_3 (167) and $CpRh(CO)_2$ (118,119). Other reagents were available commercially and were used without further purification.

Microanalyses (Table XI) and physical properties (Table X) were obtained as before.

Preparation of $CpCORh(H)Si(C_6H_5)_3$. Cyclopentadienyldicarbonylrhodium (1.12 g, 5.0 mmol) was dissolved in benzene (30 ml) and triphenylsilane (1.30 g, 5.0 mmol) added. The resulting solution was irradiated by a Hanovia 616A, 100 watt lamp for 5 days keeping the vessel close to room temperature. After filtering through a very short column of Florisil and concentrating to about 2 ml, hexane (10 ml) was added to yield off-white crystals of product (0.26 g, 0.57 mmol, 11%).

The compound $CpCORh(H)Si(CH_2C_6H_5)_3$ was produced in analogous fashion using a reaction time of one week and recrystallising the product twice from hexane. The yield of the greenish-white derivative was 0.24 g, 0.48 mmol, 10%.

Preparation of $CpCORh(SiCl_3)_2$. Cyclopentadienyldicarbonylrhodium (0.89 g, 4.0 mmol) was added to trichlorosilane

(1.37 g, 10.0 mmol). After a few seconds a vigorous reaction took place with evolution of much gas. The mixture was stirred for a further 2 hr and excess silane removed under high vacuum. The solid residue was recrystallised from hexane, sublimed under high vacuum and crystallised again from hexane. Colorless crystals of product (1.13 g, 2.43 mmol, 61%) were thus obtained.

In analogous fashion $\underline{\text{CpCORh(SiCl}_2\text{CH}_3)_2}$ was prepared using methyldichlorosilane.

Preparation of $CpCOClRhGeCl_3$. Germanium tetrachloride (0.21 g, 1.0 mmol) was added to a stirred solution of $CpRh(CO)_2$ (0.22 g, 1.0 mmol) in toluene (20 ml) and the mixture heated at 60° for 1 hr. After cooling and adding pentane (20 ml), the solid formed was recrystallised twice from dichloromethane/pentane to give the pure product (0.21 g, 0.51 mmol, 51%).

The above method, without the use of heat, was employed to obtain corresponding derivatives from the halides $GeBr_4$, $SnBr_4$, SnI_4 and CH_3SnI_3.

Preparation of $CpCOIRhGeI_3$. The compound $CpCOClRhGeCl_3$ was prepared as above from $CpRh(CO)_2$ (2.5 mmol) and $GeCl_4$ (2.6 mmol) and dissolved in dichloromethane (20 ml). Sodium iodide (1.5 g, 10 mmol) was added and the mixture stirred for 2 days. After filtration, the filtrate was concentrated to 10 ml and pentane (10 ml) added. Cooling to 0° afforded fine black crystals which were recrystallised

from dichloromethane/pentane to yield 0.82 g (1.1 mmol, 42%) of product.

Preparation of $CpCOClRhSnCl_3$. To a solution of $CpRh(CO)_2$ 0.34 g, 1.5 mmol) in pentane (20 ml) was added $SnCl_4$ (0.18 ml, 1.5 mmol), also in pentane (20 ml). A highly air-sensitive orange-yellow precipitate was formed and collected. This was allowed to decompose completely in the laboratory atmosphere and the resulting viscous oil extracted with dichloromethane (50 ml). Addition of pentane (50 ml), cooling to 0° and recrystallisation of the resulting solid from dichloromethane/pentane yielded orange-red crystals (0.24 g, 0.53 mmol, 35%).

Reactions with stannous chloride and bromide. Finely powdered stannous chloride (0.74 g, 4.0 mmol) was added to a solution of $CpRh(CO)_2$ (0.89 g, 4.0 mmol) in 1,2-dichloroethane (20 ml). The mixture was heated at 75° for 24 hr. After cooling, the precipitate was collected and dried under high vacuum to yield the orange polymeric product $[CpCORhSnCl_2]_n$ (1.26 g, 82%).

A little of this polymeric compound (0.30 g) was heated for two days in 1,2 dichloroethane (50 ml) with $CpRh(CO)_2$ (0.22 g, 1.0 mmol). After the mixture had been cooled to room temperature and filtered, pentane (20 ml) was added to the filtrate and the resulting solution cooled to -15°. Orange crystals of $[CpCORhSnCl_2.\frac{1}{3}C_2H_4Cl_2]_x$

(0.18 g, 58%) separated.

Cyclopentadienyldicarbonylrhodium (0.89 g, 4.0 mmol) was dissolved in toluene (20 ml), stannous chloride (1.5 g, 2.9 mmol) added, and the mixture stirred at 70° for 24 hr. After cooling to room temperature the mixture was filtered and the filtrate cooled to -15°. Small bright orange crystals of $\underline{[\mathrm{CpCORhSnCl_2 \cdot \frac{1}{3}C_6H_5CH_3}]_x}$ (0.41 g, 25%) were formed.

An analogous reaction takes place with stannous bromide to afford orange-red crystals of $[\mathrm{CpCORhSnBr_2 \cdot \frac{1}{3}C_6H_5CH_3}]_x$ (0.28 g, 14%).

TABLE XI

ANALYTICAL DATA

Compound	Calculated %				Found %			
	C	H	O	X	C	H	O	X
$\mathrm{CpCORh(H)Si(C_6H_5)_3}$[a]	63.19	4.64			63.44	4.47		
$\mathrm{CpCORh(H)Si(CH_2C_6H_5)_3}$[b]	65.05	5.49			65.28	5.39		
$\mathrm{CpCORh(SiCl_3)_2}$	15.50	1.08		45.76	15.64	0.92		45.54
$\mathrm{CpCORh(SiCl_2CH_3)_2}$	22.66	2.62			22.81	2.66		
$\mathrm{CpCOClRhGeCl_3}$	17.56	1.23	3.90	34.55	17.70	1.23	4.02	34.38
$\mathrm{CpCOBrRhGeBr_3}$	12.25	0.86	2.72	54.33	12.30	0.89	2.55	54.45
$\mathrm{CpCOIRhGeI_3}$	9.28	0.65	2.10	65.35	9.28	0.65	2.06	65.39
$\mathrm{CpCOClRhSnCl_3}$	15.79	1.10		31.06	15.92	1.61		31.32
$\mathrm{CpCOBrRhSnBr_3}$	11.36	0.79	2.52	50.39	11.54	0.83	2.62	50.38
$\mathrm{CpCOIRhSnI_3}$	8.76	0.61	1.95	62.94	8.91	0.58	2.08	61.68
$\mathrm{CpCOIRhSnI_2CH_3}$	11.83	1.14	2.25	53.39	11.99	1.47	2.42	53.59
$\mathrm{[CpCORhSnCl_2 \cdot \frac{1}{3}C_2H_4Cl_2]_x}$[c]	19.13	1.55		22.59	19.17	1.11		22.78
$\mathrm{[CpCORhSnCl_2 \cdot \frac{1}{3}C_6H_5CH_3]_x}$[c]	24.04	1.86	3.84	17.03	23.93	1.72	4.76	16.44
$\mathrm{[CpCORhSnBr_2 \cdot \frac{1}{3}C_6H_5CH_3]_x}$[c]	19.81	1.53	3.17	31.61	19.78	1.61	3.95	30.61
$\mathrm{[CpCORhSnCl_2]_n}$	18.69	1.31	4.15	18.39	18.51	1.76	4.23	18.35

TABLE XI (continued)

Footnotes to Table XI

[a] Confirmed by exact mass measurement on ion $CpRh(H)Si(C_6H_5)_3^+$, 428.0467 calculated; 428.0469 found. Parent ion was of very low intensity.

[b] Confirmed by exact mass measurement on parent ion $CpCORh(H)Si(CH_2C_6H_5)_3^+$, 498.0885 calculated; 498.0885 found.

[c] Compounds assumed to be trimers ($x = 3$), see discussion.

CHAPTER VI

THE REACTIONS OF CYCLOPENTADIENYL(DIMETHYLPHENYLPHOSPHINE)-CARBONYLRHODIUM WITH HALOGENS AND ORGANIC HALIDES

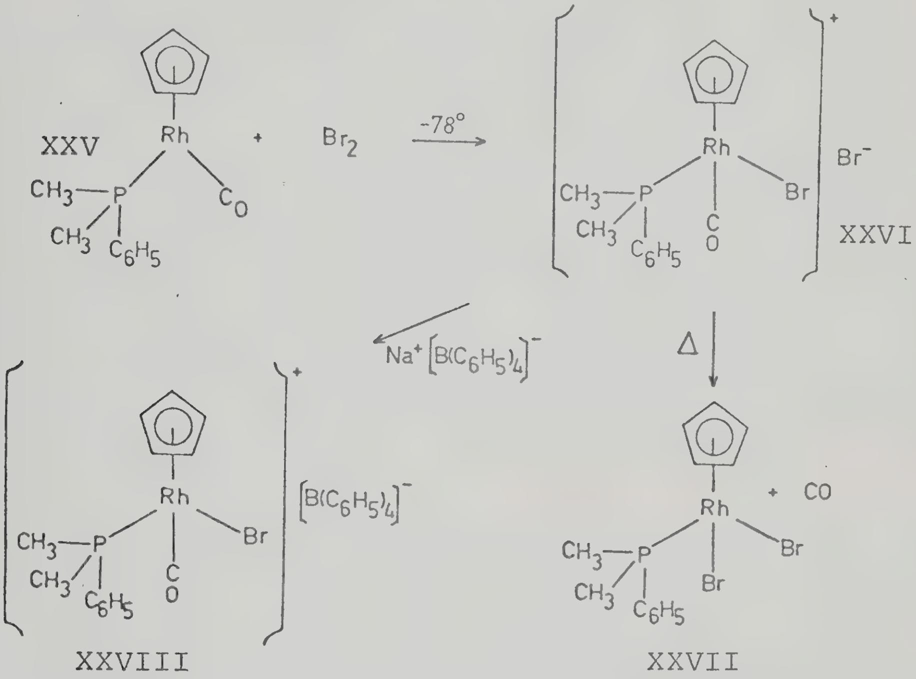
The general nature of oxidative addition reactions have been described in Chapter V. However, the tendency for d^8 complexes to undergo such reactions depends markedly on the nature of the central metal ion and the ligands associated with it. Ligands which increase electron density at the central metal improve the possibility of a complex to undergo oxidative addition (145). Thus replacement of carbon monoxide in $CpRh(CO)_2$ by a phosphine can be expected to increase the ease of oxidation of the system.

The formation of complexes $CpRh(CO)PR_3$ has been reported for a variety of phosphines (131), although no study of the reactions of such compounds has been published. The previously unreported complex with dimethylphenylphosphine was chosen for a study of oxidative-elimination processes involving halogens and pseudohalides, this particular phosphine was selected so that the formation of any compound containing an asymmetric centre at rhodium (135,136) could be monitored using the chemical shift separation of the two methyl resonances in the nmr spectrum.

RESULTS AND DISCUSSION

Bromine reacts at low temperatures with $CpRh(CO)P(CH_3)_2$-C_6H_5 (XXV) to form an ionic derivative (XXVI); on warming

to room temperature and above, the ionic form loses carbon monoxide with formation of the neutral dibromide (XXVII), (equations VI.1). The intermediate cation is stabilised by



[VI.I]

conversion to its tetraphenylboron salt (XXVIII) by rapid reaction with sodium tetraphenylboron in methanol.

Chlorine reacts similarly but the ionic derivative decomposes too rapidly to obtain an nmr spectrum. In dichloromethane solution at room temperature, infrared spectra indicate that the ionic chlorine derivative has a half-life of about two minutes. The corresponding ionic bromide decomposes more slowly as a solid or in solution. The tetraphenylboron salts of both cations are more stable, decomposing over a few days at room temperature, but they are apparently stable if stored at -15°.

On warming, both bromide and chloride ionic derivatives give high yields of nonionic dihalides. The intermediate formation of ionic halogen compounds has been observed in the preparation of other nonionic halides (168,169) and is characteristic of the general oxidative elimination reaction [V.1]. Iodine and perfluoropropyl iodide presumably react in similar fashion to chlorine and bromine but only the neutral species $CpRhP(CH_3)_2C_6H_5I_2$ and $CpRhP(CH_3)_2C_6H_5C_3F_7I$ could be isolated. Similar replacement of carbon monoxide has been noted for $CpRh(CO)_2$ (134,135). Likewise $CpCoP(C_6H_5)_3I_2$ has been formed by carbonyl replacement from $CpCo(CO)P(C_6H_5)_3$ (134).

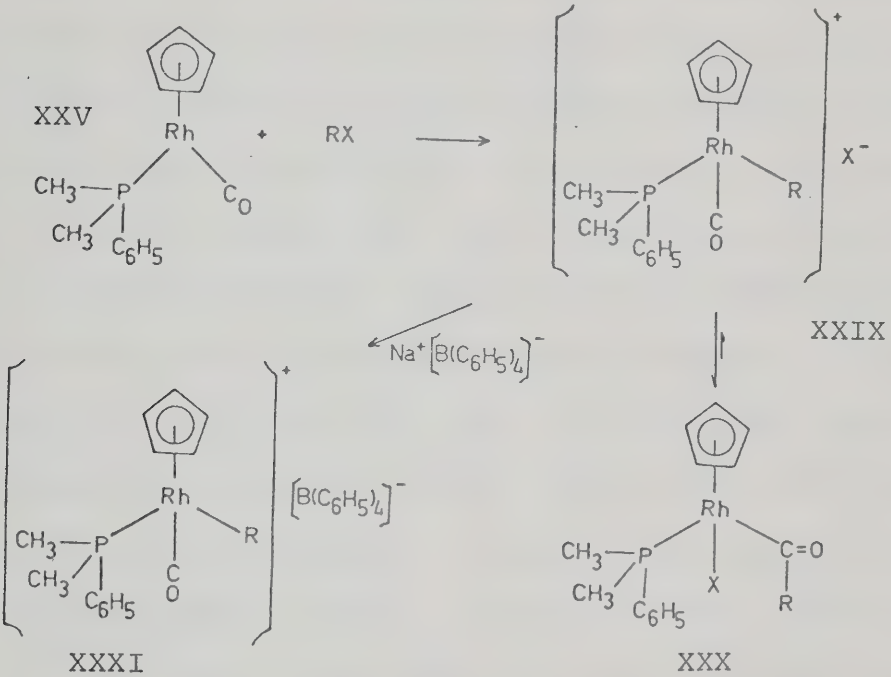
Acetyl bromide and trifluoroacetyl chloride react as pseudohalides to give ionic products at low temperature [VI.2]. These ionic compounds decompose a little below

$$CpRh(CO)P(CH_3)_2C_6H_5 + CF_3COCl \longrightarrow [CpRhP(CH_3)_2C_6H_5(CO)\text{-}COCF_3]^+Cl^- \qquad [VI.2]$$

room temperature, forming complex mixtures. Formation of tetraphenylboron derivatives only slightly increases the stability of these compounds but does give a useful method of purification. A similar derivative could not be obtained from acetyl chloride, although an infrared spectrum of the reaction mixture at -23° showed the presence of a small quantity of the desired product.

Most interesting is the reaction of $CpRhCOP(CH_3)C_6H_5$ (XXV) with alkyl halides to yield the acyl complexes

$CpRhP(CH_3)_2C_6H_5(COR)X$(XXX) [VI.3]. It appears likely that the ionic intermediate $[CpRh(CO)P(CH_3)_2C_6H_5R]^+X^-$ (XXIX) is initially formed with subsequent nucleophilic attack


XXV
Rh
CH_3—P
CH_3
C_6H_5
CO
+ RX
Rh
CH_3—P
CH_3
C_6H_5
C O
R
X^-
+
XXIX
$Na^+[B(C_6H_5)_4]^-$
Rh
CH_3—P
CH_3
C_6H_5
C O
R
+
$[B(C_6H_5)_4]^-$
XXXI
Rh
CH_3—P
CH_3
C_6H_5
X
C=O
R
XXX

[VI.3]

of the halide ion and simultaneous migration of the alkyl group to the carbonyl group. Such an intermediate must have some stability as shown by the existence of similar iridium compounds (see Chapter VII) and of $[CpRhP(CH_3)_2C_6H_5(CO)CH_3]^+$-$[B(C_6H_5)_4]^-$ (XXXI). Indeed the ease of formation of this compound could possibly be explained by the presence of an equilibrium between ionic and nonionic forms (XXIX ans XXX). Also, infrared spectral data indicate that reaction of (XXXI) with tetraphenylarsonium chloride reforms the neutral acyl compound (XXIX).

The existence of an ionic intermediate which is made neutral by halide ion attack is reminiscent of the reaction

of allyl iodide with $CpCo(CO)_2$ (170). In the latter reaction, however, both derivatives could be isolated.

Since the generalised reactions [VI.3] were originally found, two reports of similar reactions have appeared in the literature. The compound *trans*-$RhX(CO)(PR_3)_2$ reacts with methyl iodide to give initially $RhXICH_3(CO)(PR_3)_2$ (171) which slowly undergoes CO insertion to yield $RhXI(COCH_3)(PR_3)_2$. In this kinetic study there was evidence suggesting that methyl bromide undergoes the same reaction more slowly, but no analytical data were given for any products. A more careful study of *trans*-$RhCl(CO)_2PPh_3$ (172,173) has shown that this compound reacts with methyl iodide to afford $RHClI(CO)(COCH_3)PPh_3$; no intermediate could be isolated in this case.

A very limited number of alkyl halides undergo reactions [VI.3]; the steric requirement of the alkyl group seems to be an important factor. An infrared study of small scale reactions indicated that benzyl derivatives could also be formed, although no acyl carbonyl bands appeared from n-propyl chloride or t-butyl chloride reactions. A kinetic study (174) of these reactions has confirmed that the rate of reaction decreases rapidly with increasing chain length of the alkyl group and decreases with the halogen in the order I > Br > Cl. From iodobenzene and trimethyltin iodide, only the nonionic diiodide could be obtained and this in good yield in the latter case. Similar conclusions regarding the importance of steric effects were proposed in the preparation of the derivatives $CpCOP(C_6H_5)_3R_2$ (175) and

$RhXI(COCH_3)(PR_3)_2$ (171). For the rhodium compounds reported here this is consistent with the idea of initial formation of an Rh-R bond and subsequent migration of R to the carbonyl group. If the alkyl group were to bond directly to the CO carbon (e.g. in a four center mechanism), considerable easing of steric problems would be expected and the dependence of compound formation on the group R would be less easily accounted for.

It is known that attack of nucleophiles such as carbon monoxide, triphenylphosphine or iodide ion (176) on $CH_3Mn(CO)_5$ causes methyl migration to yield an acyl derivative. Such attack is analogous to the attack of halide ions on the proposed cationic intermediate $[CpRhP(CH_3)_2C_6H_5(CO)CH_3]^+$. In the rhodium system, however, attack should be even more facile due to electrostatic attraction. Indeed, the similarity of these two systems may be taken further by considering the preparation of the methyl derivatives from methyl halides. Both involve attack of a nucleophilic species $CpRh(CO)P(CH_3)_2C_6H_5$ or $Mn(CO)_5^-$ on carbon. In the former example the halide ion produced remains in solution for further reaction and in the latter the halide ion would be precipitated out, normally as the sodium salt. This mechanism can also be compared with the low temperature bromination of iron carbonyl (169), although in the present case compounds containing an acyl carbonyl are the more stable products.

Infrared Spectra. The starting material CpRh(CO)P$(CH_3)_2C_6H_5$, formally an Rh(I) compound, has a relatively low carbonyl stretching frequency which is rather sensitive to solvent (Table XII). All reactions reported here yield Rh(III) and thus in the compounds where carbon monoxide remains coordinated a typical increase in frequency is observed. When the carbon monoxide becomes placed in an acyl position, the frequency drops as expected, but remains consistent with previously known examples (171,172,177,178) of rhodium-acyl moieties. Splitting of the carbonyl bands into two components is observed in most cases. This is attributable to the extremely asymmetric nature of these molecules (44,179).

^{1}H Nmr Spectra. All spectra show at least three sets of resonances due to the phenyl and methyl protons of the phosphorus ligand and the cyclopentadienyl system attached to rhodium. Both ^{31}P and ^{103}Rh have 100% abundance in nuclei with spin ½ and thus peaks in the spectra can be expected to exhibit a double doublet structure The phenyl resonances show typical complex structures and thus only the chemical shift of the most intense line is reported for each compound in Table XIII. The methyl and cyclopentadienyl resonances do in most cases appear as the expected double doublet with phosphorus assumed to have the greater coupling constant in both cases. This seems very reasonable for the methyl groups directly attached to phosphorus but for the cyclopentadienyl systems this interpretation is based on the results of

TABLE XII

Carbonyl Stretching Frequencies [a]

Compound	ν_{CO} cm^{-1}			
$CpRhP(CH_3)_2C_6H_5(CO)$		1933[b]		
$[CpRhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$	2115 m,sh,	2100 s		
$[CpRhP(CH_3)_2C_6H_5(CO)Cl]^+B(C_6H_5)_4^-$		2105		
$[CpRhP(CH_3)_2C_6H_5(CO)Br]^+Br^-$	2109 m,sh,	2095 s		
$[CpRhP(CH_3)_2C_6H_5(CO)Br]^+B(C_6H_5)_4^-$		2099		
$[CpRhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+Br$	2079 m,sh	2061 s,	1710m,	1689 w,sh
$[CpRhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+B(C_6H_5)_4^-$	2089 w,sh,	2066 s,	1715 m	
$[CpRhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+Cl$		2081 s,	1699 m	
$[CpRhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+B(C_6H_5)_4^-$		2090 s,	1701 m	
$CpRhP(CH_3)_2C_6H_5(COCH_3)Cl$			1668 m,	1644 m
$[CpRhP(CH_3)_2C_6H_5(CO)CH_3]^+(C_6H_5)_4^-$		2068		
$CpRhP(CH_3)_2C_6H_5(COCH_3)Br$			1665 m,	1643 m
$CpRhP(CH_3)_2C_6H_5(COCH_3)I$			1662 m,	1643 m
$CpCoP(CH_3)_2C_6H_5(COCH_3)I$			1650 s,	1629 m,sh
$CpRhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl$			1660 s,	1638 m,sh
$[CpRhP(CH_3)_2C_6H_5(CO)CH_2CHCH_2]^+B(C_6H_5)_4^-$		2065		

TABLE XII (continued)

Footnotes to Table XII

[a] In dichloromethane solution.

[b] 1952 cm^{-1} in cyclohexane solution.

TABLE XIII

^{1}H NMR Spectral Data [a]

Compound	$\tau_{C_6H_5}$	τ_{Cp}	τ_x [b]	τ_{CH_3}	$\Delta\tau$ [c]	J_{P-Cp}	J_{Rh-Cp}	J_{P-X} [b]	J_{Rh-X} [b]	J_{P-CH_3}	J_{Rh-CH}
$CpRhP(CH_3)_2C_6H_5(CO)$	2.57	4.72	....	8.19	....	0.6	0.6	....	....	9.7	1.6
$CpRhP(CH_3)_2C_6H_5Cl_2$	2.48	4.70	....	7.98	....	1.8	0.5	....	....	13.1	0.7
$[CpRhP(CH_3)_2C_6H_5(CO)$- $Br]^+Br^-$	2.42	3.57	....	7.37	0.10	1.5	0.4	....	....	12.6	0[d]
$CpRhP(CH_3)_2C_6H_5Br_2$	2.50	4.70	....	7.85	....	1.7	0.4	....	....	12.3	0.7
$CpRhP(CH_3)_2C_6H_5I_2$	2.50	4.63	....	7.65	....	1.8	0[d]	....	....	11.6	0.7
$CpRhP(CH_3)_2C_6H_5C_3F_7I$[e]	2.52	4.75	....	7.89	0.18	1.5	0	....	....	10.6	0
$[CpRhP(CH_3)_2C_6H_5(CO)$- $(COCH_3)]^+Br^-$[f]	2.48	3.92	7.48	7.61	0.11	1.0	0.4	0	0	11.9	1.2
$[CpRhP(CH_3)_2C_6H_5(CO)$- $(COCH_3)]^+B(C_6H_5)_4$	3.07	4.68	7.58	8.13	0.07	1.1	0.4	0	0	11.6	1.1
$[CpRhP(CH_3)_2C_6H_5(CO)$- $(COCF_3)]^+Cl^-$	2.44	3.66	....	7.41	0.07	0	0	....	....	12.4	0
$[CpRhP(CH_3)_2C_6H_5(CO)$- $(COCF_3)]^+B(C_6H_5)_4^-$	3.10	4.87	....	8.27	0.04	1.2	0.4	....	....	11.5	1.1
$CpRhP(CH_3)_2C_6H_5$- $(COCH_3)Cl$	2.20	4.84	7.18	8.17	0.17[h]	1.5	0.6	0.4	0	11.7	1.3
$[CpRhP(CH_3)_2C_6H_5(CO)$- $CH_3]^+B(C_6H_5)_4$	3.08	4.85	9.18	8.35	0.04	1.3	0.4	5.1	2.2	11.2	1.1

TABLE XIII (continued)

$CpRhP(CH_3)_2C_6H_5$- $(COCH_3)Br$	2.53	4.70	7.08	8.08	0.10[h]	1.6	0.6	0.4	0	11.4	1.1
$CpRhP(CH_3)_2C_6H_5$- $(COCH_3)I$	2.55	4.75	7.02	7.99	0.02[h]	1.6	0.6	0	0	11.2	1.3
$CpRhP(CH_3)_2C_6H_5$- $(COCH_2CHCH_2)Cl$	2.56	4.82		8.18	0.16[i]	1.4	0.6	....	....	11.8	1.2
$[CpRhP(CH_3)_2C_6H_5$- $(CH_2CHCH_2)(CO)]^+B(C_6H_5)_4^-$	3.11	4.88		8.32	0.03	1.1	0.4	....	....	11.4	1.2

---

[a] Measured at 60 Mc at 40° in $CDCl_3$ soln. except $B(C_6H_5)_4^-$ salts in CD_2Cl_2 soln.

[b] τ_{CH_3} refers to protons of methyl groups not directly bonded to phosphorus.

[c] $\Delta\tau$ refers to the chemical shift separation of the two phosphorus methyl groups due to the asymmetric centre on rhodium.

[d] A value of 0 c.p.s. normally indicated a coupling constant of <0.4 c.p.s. which could not be resolved by the spectrometer used.

[e] This compound showed some broadening of the resonance lines presumably due to fluorine coupling.

[f] Spectrum obtained at 0°.

[g] Spectrum obtained at -20° poorly resolved.

[h] Spectrum also measured at 100 Mc in order to differentiate chemical shift separations from rhodium coupling.

[i] Chemical shift separation dependent on temperature; at -40°, $\tau_{\mathrm{Sepn.}} = 0.23$.

Schuster-Woldan and Basolo (131) and the results given in Chapter VIII. Spectral measurements on the compound $CpRhP(C_6H_5)_3(CH_3)_2$ (137) also agree in this relative assignment although this work must be treated with caution (see Chapter V). In the Rh(I) compound (XXV) the phosphorus and rhodium couplings to the cyclopentadienyl ring are of the same order with the result that a triplet is observed, just as in the compound $CpRh(CO)P(C_6H_5)_3$ (131). Little can be inferred from the small changes in τ_{cp} except to note the deshielding present in the ionic halides in chloroform solution.

Because of ^{31}P and ^{103}Rh coupling the two methyl groups are expected to appear in the nmr spectra as double doublets, as noted above; in addition, the difference in magnetic environment of each group due to the asymmetry at rhodium, in most derivatives reported here, introduces a chemical shift separation ($\Delta\tau$). Thus a group of eight equally intense lines should be observed. This was experimentally verified, but did introduce the problem of correctly interpreting separation as chemical shifts or coupling constants. Three representative spectra of $CpRhP(CH_3)_2C_6H_5(COCH_3)X$, where X = Cl (Figure 17), Br (Figure 18) or I (Figure 19) were observed at 100 Mc as well as 60 Mc, thus providing unambiguous assignments in these cases and allowing fairly confident assignments to be made for the other compounds. Similar uses of magnetic nonequivalence of methyl groups to confirm asymmetry have been reported for the compounds $CpFe(CO)(COCH_3)$-

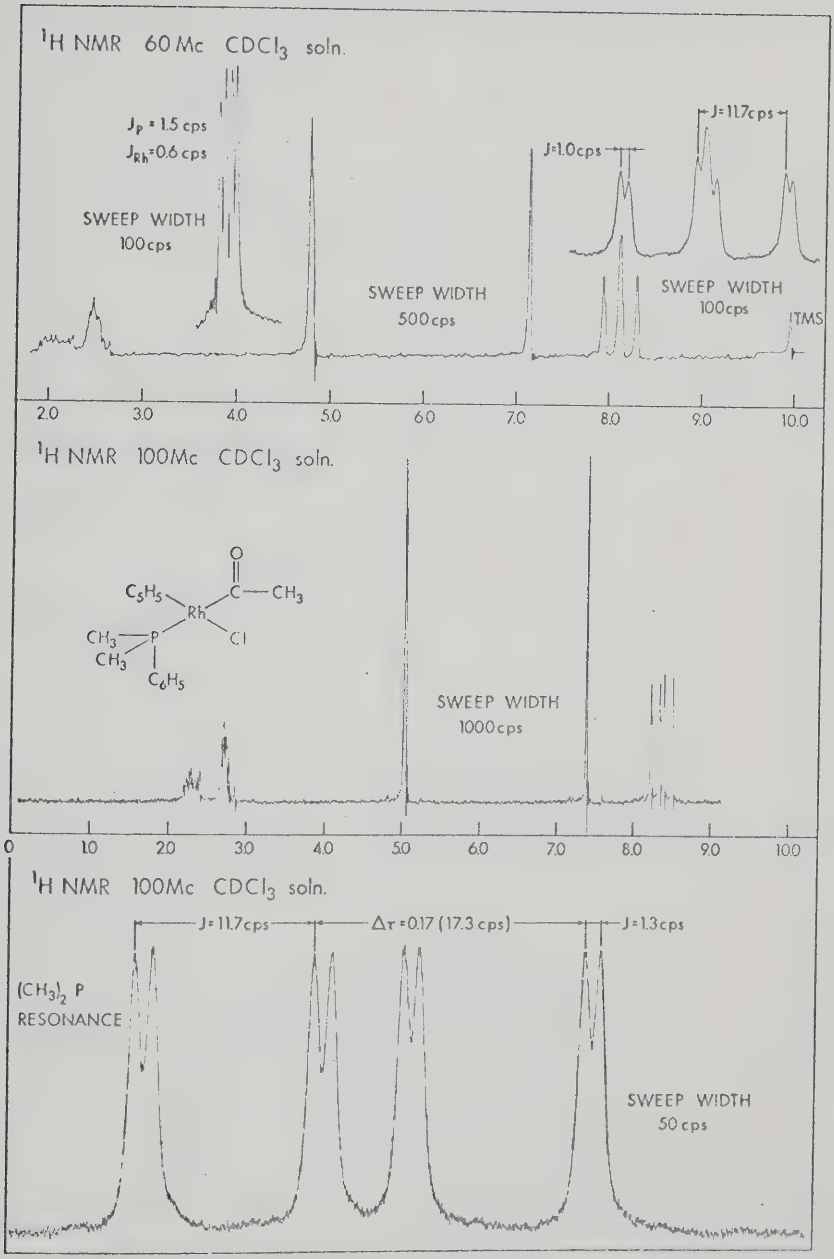


FIGURE 17: The ^{1}H NMR Spectrum of CpRhP-$(CH_3)_2C_6H_5(COCH_3)Cl$.

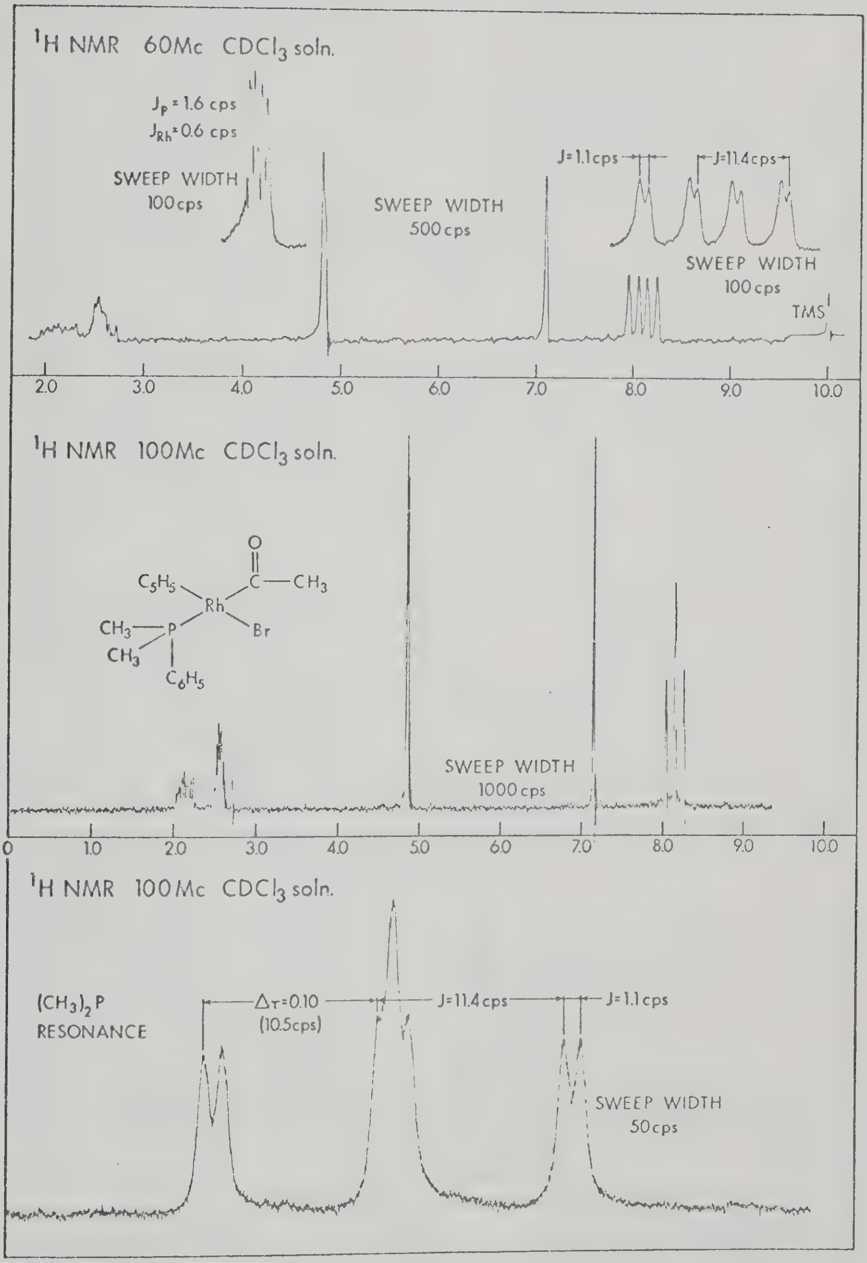


FIGURE 18. The ^{1}H NMR Spectrum of $CpRhP(CH_3)_2C_6H_5(COCH_3)Br$.

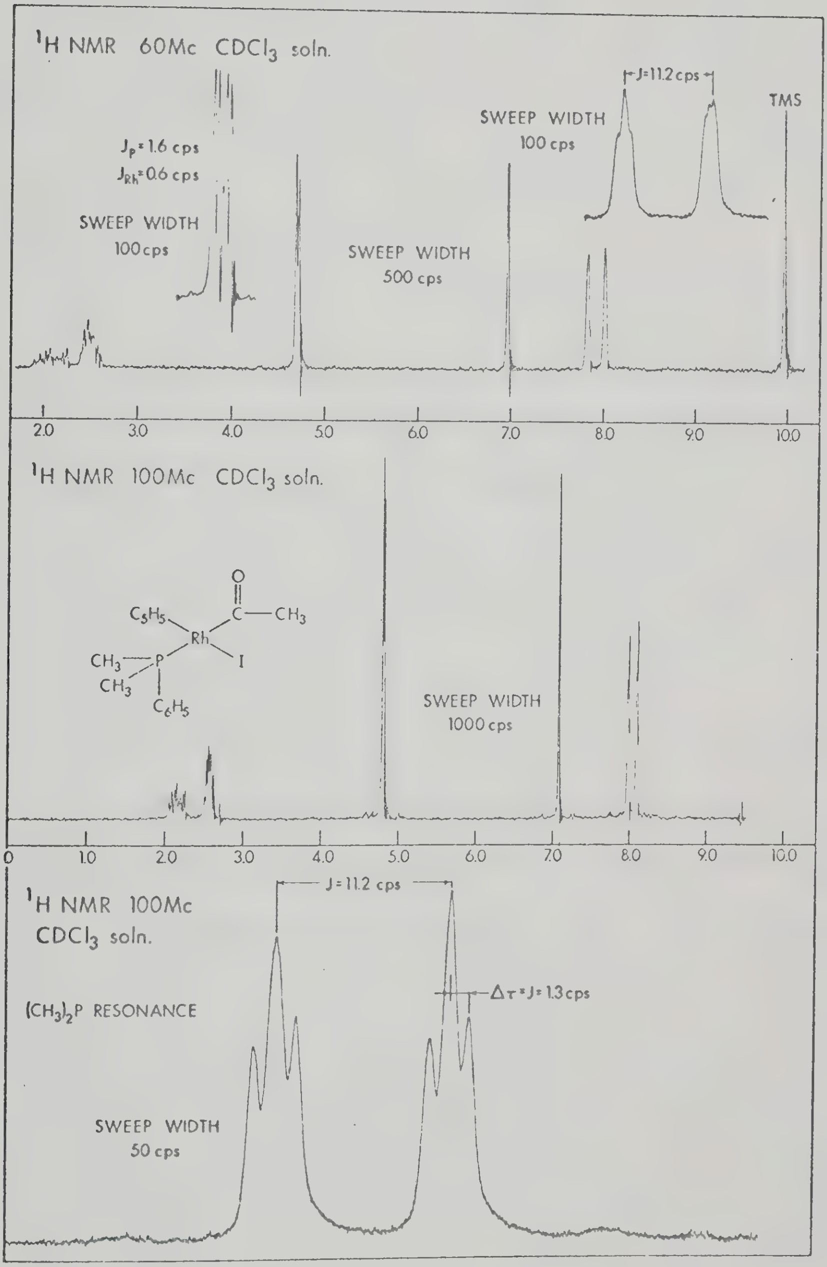


FIGURE 19: The ^{1}H NMR Spectrum of

$CpRhP(CH_3)_2C_6H_5(COCH_3)I$.

$P(CH_3)_2C_6H_5$ (180) and $CpFe(CO)P(C_6H_5)_3CH_2Si(CH_3)_2C_6H_5$ (181).

Values of J_{P-CH_3} (Table XIII) are greater in the Rh(III) derivatives than in the Rh(I) starting material; this is in accord with the view that the effective electronegativity of Rh(III) is greater. Decreasing J_{P-CH_3} along the series chloro, bromo and iodorhodium (III) derivatives can similarly be rationalised.

Other resonances observed were attributed to acyl groups which appeared at chemical shifts expected for such groups (171,178), and in the compound $[CpRhP(CH_3)_2C_6H_5(CO)CH_3]^+[B(C_6H_5)_4]^-$ (Figure 20) a methyl group is directly attached to rhodium. The observed chemical shift and coupling constants are comparable in magnitude to such compounds as $RhCl_2CH_3(CO)[P(C_6H_5)_3]_2$ (178) where $\tau_{CH_3} = 9.15$ $J_{P-CH_3} = 5.0$ cps and $J_{Rh-CH_3} = 2.1$ cps. The resonances exhibited by allyl protons were insufficiently resolved for determination of the associated nmr parameters. Relative peak areas were found to be correct for all compounds. The only exception was the ionic σ-allyl complex, where integration was not possible, for the allyl protons showed their presence only by small deviations from a straight base line. The other protons in the molecule integrated correctly.

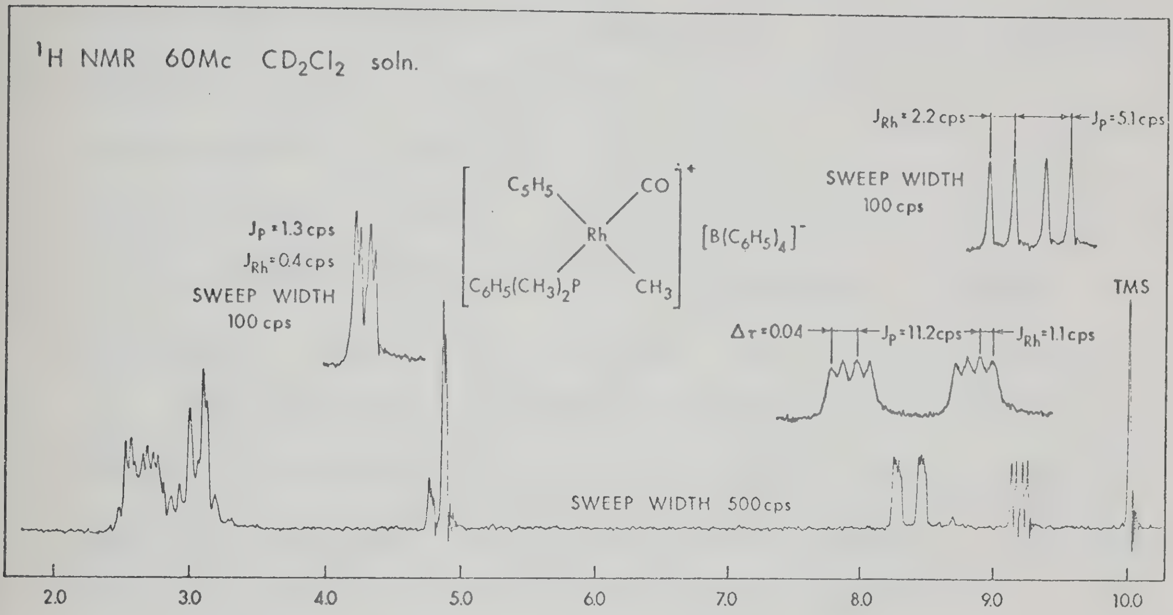


FIGURE 20: The ^{1}H NMR Spectrum of $[CpRhP(CH_3)_2C_6H_5(CO)CH_3]^+$-$[B(C_6H_5)_4]^-$

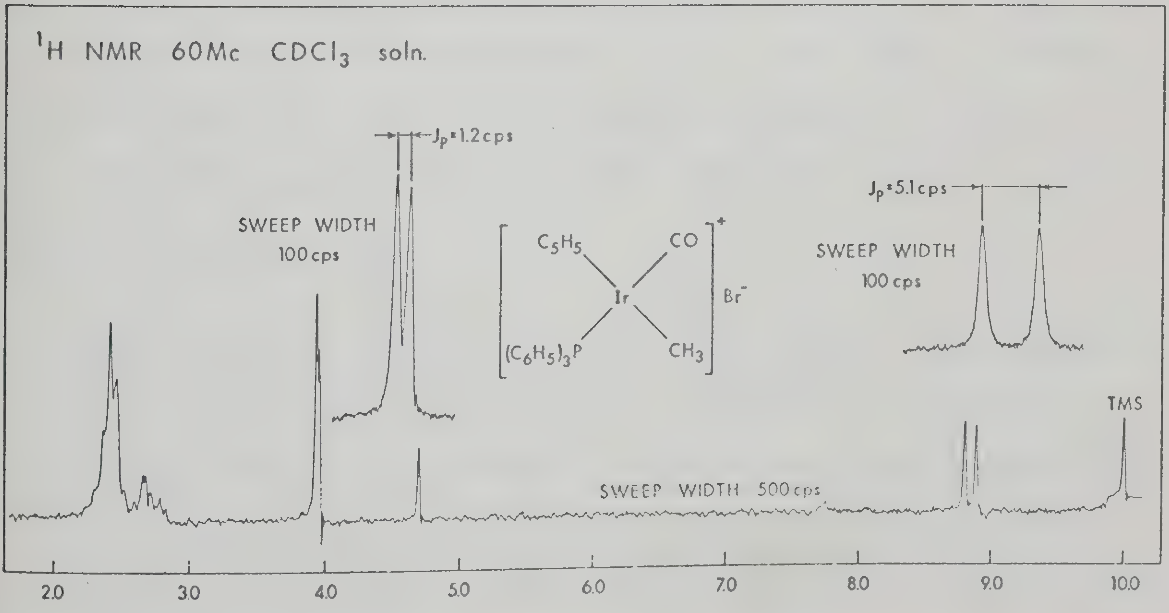


FIGURE 21: The ^{1}H NMR Spectrum of $[CpIrP(C_6H_5)_3(CO)CH_3]^+Br^-$.

EXPERIMENTAL SECTION

Analyses (Table XIV) and nmr spectra (Table XIII) were obtained as given in Chapter II. Infrared spectra (Table XII) were measured with a Perkin-Elmer 337 grating spectrometer and recorded in expanded form on a Hewlett-Packard 7127A recorder. Spectra were calibrated using a carbon monoxide gas cell for the terminal carbonyl region and a polystyrene film for acyl carbonyl spectra.

Solvents were purified as described previously. Halogens and organic halides were used as obtained from commercial sources, except the organic iodides, which were distilled after standing over sodium thiosulfate.

Preparation of $CpRh(CO)P(CH_3)_2C_6H_5$. Cyclopentadienyldicarbonylrhodium (1.27 g, 5.7 mmol) was dissolved in hexane (50 ml) and phenyldimethylphosphine (1.0 g, 7.2 mmol) added. The mixture was stirred for 6 hr at room temp, filtered, and cooled to -15°. Fine orange crystals of product slowly formed and were filtered off and dried in vacuum (yield 1.2 g, 63%).

Preparation of $[CpRhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$. A solution of $CpRh(CO)P(CH_3)_2C_6H_5$ (0.33 g, 1.0 mmol) in 10 ml of dichloromethane was cooled to liquid nitrogen temperature and chlorine (0.07 g, 1.0 mmol) was distilled in. The mixture was slowly warmed to -78° and hexane (15 ml) added

to precipitate a bright yellow solid. The solution was decanted and the solid washed twice with 10-ml portions of hexane, while maintaining the temperature close to -78°. After drying under high vacuum for several hours, the yield of product was 0.35 g (86%).

A similar procedure was used to prepare $[CpRhP(CH_3)_2C_6H_5(CO)Br]^+Br^-$, 24 hr was allowed for the reaction with bromine at -78°.

Reaction of the phosphine adduct with CH_3COBr and CF_3COCl in similar fashion afforded $[CpRhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+Br^-$ and $[CpRhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+Cl^-$; these reactions were carried out at -23° for 12 hr, and during the work-up procedure the temperature was maintained near -23°.

Preparation of $[CpRhP(CH_3)_2C_6H_5(CO)Cl]^+[B(C_6H_5)_4]^-$. The chloride $[CpRhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$ (0.20 g, 0.49 mmol) was quickly dissolved in methanol (10 ml) and a solution of sodium tetraphenylboron (0.25 g, 0.73 mmol) in 5 ml of methanol immediately added. The mixture was stirred for 30 min and the bright yellow precipitate which formed was filtered off. This was washed twice with 3-ml portions of methanol, once with 3 ml of pentane and dried under vacuum. The weight of product was 0.27 g, (80%).

The compounds $[CpRhP(CH_3)_2C_6H_5(CO)Br]^+[B(C_6H_5)_4]^-$
$[CpRhP(CH_3)_2C_6H_5(CO)(COCH_3)]^+[B(C_6H_5)_4]^-$
$[CpRhP(CH_3)_2C_6H_5(CO)(COCF_3)]^+[B(C_6H_5)_4]^-$ were prepared

by the procedure outlined above from the corresponding halide salts.

Preparation of $CpRhP(CH_3)_2C_6H_5Cl_2$. The ionic halide $[CpRhP(CH_3)_2C_6H_5(CO)Cl]^+Cl^-$ (0.20 g, 0.49 mmol) was placed in 10 ml of dichloromethane and stirred for 6 hr. Hexane (20 ml) was added and the mixture cooled to yield $CpRhP(CH_3)_2C_6H_5Cl_2$ (0.16 g, 86%).

The corresponding dibromide $CpRhP(CH_3)_2C_6H_5Br_2$ was also prepared by this method from $[CpRhP(CH_3)_2$-$C_6H_5(CO)Br]^+Br^-$; however, a reaction time of 3 days was necessary for complete conversion in this case.

Preparation of $CpRhP(CH_3)_2C_6H_5I_2$. A sample of CpRh(CO)-$P(CH_3)_2C_6H_5$ (0.22 g, 0.66 mmol) was dissolved in 20 ml of dichloromethane and iodine (0.17 g, 0.66 mmol) added. After 1 hr, the solution was concentrated to 5 ml, 10 ml of pentane was added, and the mixture was cooled to -10°. The fine black needles of product which formed were collected and dried (yield 0.27 g, 73%).

Preparation of $CpRhP(CH_3)_2C_6H_5C_3F_7I$. Perfluoropropyl iodide (2.0 g, 6.8 mmol) was added to $CpRh(CO)P(CH_3)_2C_6H_5$ (0.50 g, 1.5 mmol) dissolved in 10 ml hexane and the mixture allowed to stand for 24 hr. The orange microcrystalline precipitate was collected, washed with two 10-ml portions of hexane and dried (yield 0.53 g, 59%).

Preparation of $CpRhP(CH_3)_2C_6H_5(COCH_3)Cl$. A sample of

$CpRh(CO)P(CH_3)_2C_6H_5$ (0.44 g, 1.3 mmol) was placed in a Carius tube and about 2 ml of methyl chloride condensed into the tube. After sealing, the tube was left at room temperature for 4 days. Excess methyl chloride was removed under reduced pressure, and the product was collected and recrystallized twice from dichloromethane-pentane (yield, 0.24 g, 48%).

Reactions with methyl bromide and allyl chloride were carried out by a similar procedure for a period of 24 hr; the products were $\underline{CpRhP(CH_3)_2C_6H_5(COCH_3)Br}$ and $\underline{CpRhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl}$ respectively.

Preparation of $[CpRhP(CH_3)_2C_6H_5(CO)CH_3]^+[B(C_6H_5)_4]^-$. A solution of sodium tetraphenylboron (0.25 g, 0.73 mmol) in 5 ml of methanol was added slowly to $CpRhP(CH_3)_2C_6H_5(COCH_3)Cl$ (0.19 g, 0.5 mmol) in 10 ml of methanol. A pale orange precipitate formed immediately, but this quickly became white. After stirring for 1 hr the precipitate was filtered off, washed twice with 5-ml portions of methanol and once with 5 ml of pentane. After drying in vacuum, the yield of microcrystalline white product was 0.32 g (96%).

The same procedure was used to form the very pale yellow $\underline{[CpRhP(CH_3)_2C_6H_5(CO)CH_2CHCH_2]^+[B(C_6H_5)_4]^-}$ from $CpRhP(CH_3)_2C_6H_5(COCH_2CHCH_2)Cl$.

Preparation of $CpRhP(CH_3)_2C_6H_5(COCH_3)I$. Methyl iodide (0.34 g, 2.4 mmol) was added to a solution of CpRh(CO)-

$P(CH_3)_2C_6H_5$ (0.33 g, 1.0 mmol) in 20 ml of dichloromethane and the mixture stirred for 1 hr. The solution was concentrated to about 1 ml and hexane added very slowly to yield dark red crystals (0.34 g, 71%).

The cobalt derivative $\underline{CpCoP(CH_3)_2C_6H_5(COCH_3)I}$ was prepared by a similar method from $CpCo(CO)P(CH_3)_2C_6H_5$. The latter was formed by refluxing $CpCo(CO)_2$ with excess phosphine in hexane solution.

TABLE XIV

Analytical Data, Melting Points, Colors and Yields

Compound	Mp, °C[a]	Color	% yield	Calculated %				Found %			
				C	H	X	P	C	H	X	P
$CpRhP(CH_3)_2C_6H_5(CO)$	78-80	Orange	63	50.32	4.83	....	....	50.21	4.83	....	....
$[CpRhP(CH_3)_2C_6H_5(CO)\text{-}Cl]^+Cl^-$	b	Yellow	86	....	...	....	....	.....	....	....	....
$[CpRhP(CH_3)_2C_6H_5(CO)\text{-}Cl]^+B(C_6H_5)_4^-$	94-97 dec	Pale yellow	80	66.25	5.27	....	....	66.11	5.21	....	....
$CpRhP(CH_3)_2C_6H_5Cl_2$	245-248	Dark red	86	41.41	4.28	18.81	8.21	41.23	4.40	18.66	8.08
$[CpRhP(CH_3)_2C_6H_5(CO)\text{-}Br]^+Br^-$	95-97	Orange	98	34.04	3.26	32.35	....	33.96	3.53	32.51	...
$[CpRhP(CH_3)_2C_6H_5(CO)\text{-}Br]^+B(C_6H_5)_4^-$	87-92 dec	Yellow-orange	90	62.24	4.95	....	....	62.21	4.89	....	...
$CpRhP(CH_3)_2C_6H_5Br_2$	222-226 dec	Dark red	80	33.51	3.46	34.30	6.65	33.14	3.63	34.46	6.53
$CpRhP(CH_3)_2C_6H_5I_2$	204-206	Black	73	27.88	2.88	45.35	5.53	27.77	3.04	45.45	5.39
$CpRhP(CH_3)_2C_6H_5C_3F_7I$	123-125	Orange	59	31.92	2.68	....	....	31.76	2.91	....	....
$[CpRhP(CH_3)_2C_6H_5(CO)\text{-}(COCH_3)]Br^-$	b	Yellow	83	.....	....	....	....	....	....	....	....
$[CpRhP(CH_3)_2C_6H_5(CO)\text{-}(COCH_3)]^+B(C_6H_5)_4^-$	98-100 dec	Yellow	70	68.98	5.64	....	....	68.77	5.77	....	....

TABLE XIV (continued)

$[CpRhP(CH_3)_2C_6H_5CO)-(COCF_3)]^+Cl^-$	b	Pale Yellow	86	...	...	...	...	...	...	...	...
$[CpRhP(CH_3)_2C_6H_5(CO)-(COCF_3)]^+B(C_6H_5)_4^-$	102-103 dec	White	80	64.02	4.84	...	...	63.96	4.85	...	...
$CpRhP(CH_3)_2C_6H_5-(COCH_3)Cl$	92-94	Dark red	48	46.84	4.98	9.22	4.16[c]	47.13	4.87	8.98	4.06[c]
$[CpRhP(CH_3)_2C_6H_5(CO)-CH_3]^+B(C_6H_5)_4^-$	130 dec	White	96	70.08	5.88	...	4.63	70.10	5.91	...	4.85
$CpRhP(CH_3)_2C_6H_5-(COCH_3)Br$	118-122	Dark red	51	41.99	4.46	18.62	3.73[c]	41.98	4.21	18.50	3.89[c]
$CpRhP(CH_3)_2C_6H_5-(COCH_3)I$	113-115	Dark red	71	37.84	4.02	26.65	6.51	36.40	4.04	27.32	6.52
$CpCoP(CH_3)_2C_6H_5-(COCH_3)I$	98-100	Black	76	41.69	4.20	...	...	41.51	4.51	...	...
$CpRhP(CH_3)_2C_6H_5-(COCH_2CHCH_2)Cl$	109-112	Dark red	46	49.72	5.15	...	...	49.37	5.27	...	...
$[CpRhP(CH_3)_2C_6H_5CO)-(CH_2CHCH_2)]^+B(C_6H_5)_4^-$	106-108 dec	Pale Yellow	91	70.90	5.95	...	...	70.73	6.37	...	...

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[a] All melting points determined using Kofler hot stage

[b] Compound decomposes below room temperature.

[c] Refers to O not P analysis.

CHAPTER VII

NUCLEOPHILIC PROPERTIES OF CYCLOPENTADIENYL(TRIPHENYLPHOSPHINE)CARBONYLIRIDIUM

Some oxidative addition reactions on CpRh(CO)P$(CH_3)_2$-C_6H_5 have been described in Chapter VI, and so it seemed a similar study of a corresponding iridium compound might prove fruitful. The compound chosen was the triphenylphosphine derivative CpIr(CO)P$(C_6H_5)_3$ since this could be very conveniently prepared as described below.

The strong resemblance of CpCo$(CO)_2$ and Fe$(CO)_5$ has often been noted (182,162) and thus the phosphine-substituted cyclopentadienyldicarbonyl compounds of rhodium and iridium might usefully be compared with the phosphine substituted pentacarbonyls of ruthenium and osmium e.g. Ru$(CO)_3$[P$(C_6H_5)_3]_2$. The oxidative addition reactions of the latter systems have been well studied by Collman and Roper (168,183,184). Osmium compounds were found to give stable ionic derivatives, e.g. $\{OsBr(CO)_3[P(C_6H_5)_3]_2\}^+Br^-$, as intermediates in the formation of the neutral dihalide (168). No such ionic intermediates could be isolated for the analogous ruthenium systems (183). This was attributed to the heavier transition metal having more strongly bound carbonyl groups (168,185). In comparison, CpRhP$(CH_3)_2$-C_6H_5(CO) reacts with halogens to give unstable ionic intermediates which could only be isolated with difficulty. It might be expected, therefore, that comparable iridium complexes would give stable ionic derivatives and this has been

borne out by the work reported here.

RESULTS AND DISCUSSION

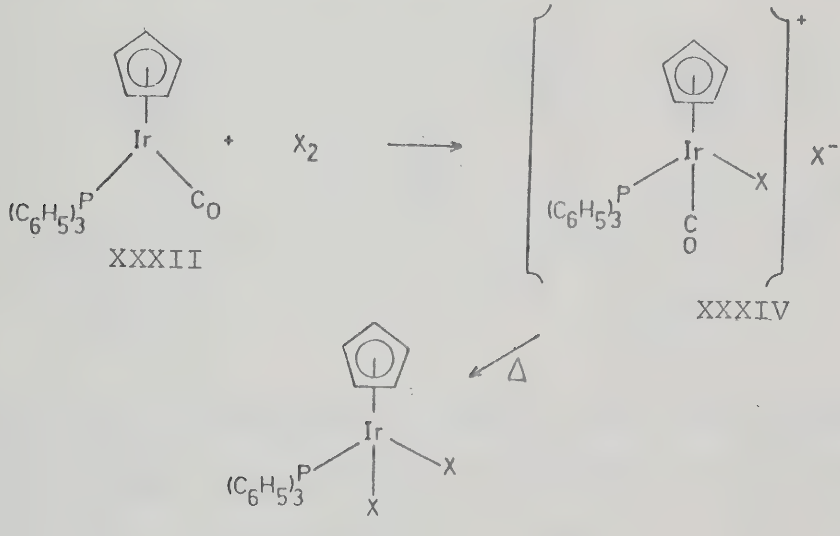
Cyclopentadienyltriphenylphosphinecarbonyliridium (XXXII) has been reported to form by the slow reaction of $CpIr(CO)_2$ (XXXIII) with triphenylphosphine. However, in this kinetic study (131) the product was poorly characterised. Thus using $P(C_6H_5)_3$ and XXXIII prepared by the procedure of Fischer and Brenner (120) high yields of XXXII could be expected. Unfortunately the required intermediate, $Ir(CO)_3Cl$, is obtained in good yield only by a difficult and very tedious route.

It was then discovered that treating the well known and easily prepared (152) compound $[(C_6H_5)_3P]_2Ir(CO)Cl$ with sodium cyclopentadienide gave XXXII simply and efficiently [VII.1]. This reaction involves the displacement of a phosphine ligand by the olefinic system, which is similar to the recently reported preparation of $CpCo[P(C_6H_5)_3]_2$ (186) from $[(C_6H_5)_3P]_3Co(N_2)H$ and cyclopentadiene. The derivative $CpRh(CO)P(C_6H_5)_3$ may likewise be formed by the reaction of sodium cyclopentadienide with $[(C_6H_5)_3P]_2Rh(CO)Cl$ (160). The latter may be produced in high yield from $RhCl_3$ via Wilkinson's compound $[(C_6H_5)_3P]_3RhCl$ (160). It is doubtful if this method has any advantage compared to the known procedure which uses cyclopentadienyldicarbonyl-

$$[(C_6H_5)_3P]_2Ir(CO)Cl + C_5H_5Na \longrightarrow CpIr(CO)P(C_6H_5)_3 + NaCl + P(C_6H_5)_3 \qquad [VII.1]$$

rhodium and triphenylphosphine (131,174). The reactions were not carried out in tetrahydrofuran, in which the sodium cyclopentadienide was prepared, since compound XXXII was found to decompose in this solvent.

Halogens readily react with solutions of XXXII to form ionic derivatives (XXXIV) without evolution of carbon monoxide [VII.2]. The compounds (XXXIV) are very stable compared to similar ionic halides and except for the chloride show no decomposition at room temperature. The reaction requires equimolar ratios or a slight excess of XXXII to eliminate formation of the complex anions Br_3^- and I_3^-. The ionic nature of XXXIV was confirmed in each case by the immediate formation of a precipitate on reaction with solutions of sodium tetraphenylboron in methanol. In less polar solvents the compounds (XXXIV) were almost insoluble, and this prevented the observation of nmr spectra in the solvents $CDCl_3$ or CCl_4.



XXXII

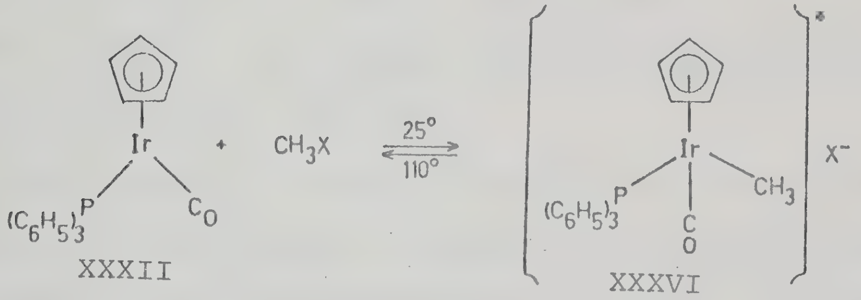
XXXIV

XXXV

[VII.2]

On refluxing a suspension of any one of these ionic halides in toluene, carbon monoxide was evolved to afford a neutral dihalide (XXXV) with some decomposition. The compounds (XXXV) were very stable and quite soluble in moderately polar solvents.

The reactions of methyl halides with the iridium complex (XXXII) also yield ionic products $[CpIrP(C_6H_5)_3(CO)CH_3]^+ X^- \cdot \frac{1}{2}CH_2Cl_2$ (XXXVI) [VII.3]. The presence of solvent in the crystals was confirmed by analysis and nmr spectroscopy. A limited number of other alkyl halides undergo this reaction, for which a kinetic study has been made (174). Some steric restrictions seem to apply although they are not so severe as in analogous rhodium reactions. There can be little restriction on chain length, for n-hexyl iodide yields a stable product. Under the same conditions infrared spectroscopy gives no evidence of the required product with isopropyl iodide. Thus the reaction seems limited to primary halides.



XXXII XXXVI [VII.3]

Typical of nucleophilic attack on alkyl halides the rate of reaction is in the order I > Br > Cl (187) and a product is formed easily with the activated benzyl iodide.

These ionic alkyliridium complexes tend to form oils in their preparation but solids result using the solvent mixtures dichloromethane/diethyl ether or dichloromethane/benzene rather than dichloromethane/hexane. The presence of dichloromethane in the crystals appeared independent of the three possible mixtures used for recrystallisation and even high vacuum did not remove this solvent. It remains unclear why dichloromethane is held strongly in the crystal lattice of most alkyl halide derivatives but is not retained by the derivatives of benzyl iodide or perfluoropropyl iodide or the ionic dihalides.

The reaction of methyl iodide with a similar rhodium system was found to give a neutral acyl compound $CpRhP(CH_3)_2$-$C_6H_5(COCH_3)I$ [IV.3] presumably via an ionic intermediate analogous to the complex (XXXVI). Use of heat to encourage the nucleophilic attack of iodide ion on $[CpIrP(C_6H_5)_3(CO)$-$CH_3]^+$ might also be expected to give an acyl compound; however, refluxing in toluene was found, by observing the carbonyl absorption frequency, to give a high yield of XXXII. It seems reasonable that an equilibrium between the compounds XXXII and XXXVI [VII.3] is displaced by removal of methyl iodide into the gas phase and this results in the reforming of XXXII.

The nucleophilic character of XXXII is evident from the reactions already mentioned but is greatly emphasised by treatment with acids. The protonation of d^8 complexes by strong acids is well known (168,184,188). The compound

(XXXII) is shown by a shift in the carbonyl stretching frequency to 2063 cm^{-1} to be protonated by most moderately strong acids. Silicotungstic acid as would be expected (30) gives an immediate precipitate on reaction with XXXII in acetone solution. Derivatives with the oxidising acids, perchloric and sulfuric, rapidly decompose and those with halogen acids dissociate in solution. A pure product could be obtained, however, using hydrogen bromide and quickly reacting the protonated compound with sodium tetraphenylboron.

Lewis acids were similarly found to form adducts with XXXII. Boron and aluminum trichlorides afford products which could not be isolated in a pure state but adducts were characterised with zinc bromide, mercuric chloride and thallic chloride. In forming these adducts it is necessary to use exactly equimolar ratios, since purification of the products is very difficult. Kemmitt and coworkers (110,111,189) have shown that a number of d^8 compounds can form adducts with mercuric halides and of particular interest is the related iridium adduct $CpIr(C_8H_{12})\cdot HgCl_2$ (110). Adducts with zinc and thallium compounds are unusual since few such complexes have been formed between these metals and any transition metal (190).

Infrared Spectra. The compound XXXII exhibits a single carbonyl absorption at the same frequency as that of an authentic sample of $CpIrP(C_6H_5)_3(CO)$ prepared from $CpIr(CO)_2$ and $(C_6H_5)_3P$. This is at a frequency (Table XV) below the rhodium analogue as seems to be usual for the carbonyls of third-row transition metals compared to second row (131, 185). This has been attributed to the lanthanide contraction in the Group VI hexacarbonyls (185) and such an explanation should be equally valid for Group VIII carbonyls.

The formation of ionic derivatives of XXXII and consequent increase in formal oxidation state and effective electronegativity of iridium causes the usual increase in the carbonyl stretching frequencies (191). The extent of this increase is affected by the electron-withdrawing ability of the added substituent on the metal; the change, observed to be in the order $Cl > Br > I > H > CH_3 > R$, could therefore have been predicted.

The adducts with $ZnBr_2$, $HgCl_2$ and $TlCl_3$ also show increases in carbonyl stretching frequencies depending on the acidity of these halides; Lewis acids can be expected to remove charge from iridium although there is no formal increase in oxidation state of iridium. The spectra of the adducts were taken in acetone and Nujol mulls as well as the ubiquitous dichloromethane so that comparisons could be made with such derivatives as $CpRh(CO)_2 \cdot HgCl_2$ and $CpCo(CO)_2 \cdot HgCl_2$ (110, 183). The latter derivatives were found to dissociate in acetone, whereas this is not so for $CpIrP(C_6H_5)_3(CO) \cdot HgCl$. This may be attributed to the

TABLE XV

Physical Properties and Carbonyl Stretching Frequencies

Compound	m.p.°C	Color	% Yield	Solvent for ν_{CO},cm^{-1}	
$CpIrP(C_6H_5)_3(CO)$	160	Orange	60	C_6H_{12}	1944
				CH_2Cl_2	1926
$[CpIrP(C_6H_5)_3(CO)Cl]^+Cl^-$		Pale-Yellow	86	CH_2Cl_2	2088
$CpIrP(C_6H_5)_3Cl_2$	290	Yellow	26		
$[CpIrP(C_6H_5)_3(CO)Br]^+Br^-$	140	Yellow	93	CH_2Cl_2	2085
$CpIrP(C_6H_5)_3Br_2$	275	Orange	31		
$[CpIrP(C_6H_5)_3(CO)I]^+I^-$	110	Orange	85	CH_2Cl_2	2079
$CpIrP(C_6H_5)_3I_2$	290	Red	41		
$[CpIrP(C_6H_5)_3(CO)CH_3]^+Cl^-.\frac{1}{2}CH_2Cl_2$	170	White	77	CH_2Cl_2	2049
$[CpIrP(C_6H_5)_3(CO)CH_3]^+Br^-.\frac{1}{2}CH_2Cl_2$	180	White	84	CH_2Cl_2	2049
$[CpIrP(C_6H_5)_3(CO)CH_3]^+I^-.\frac{1}{2}CH_2Cl_2$	180	White	89	CH_2Cl_2	2050
$[CpIrP(C_6H_5)_3(CO)C_2H_5]^+I^-.\frac{1}{2}CH_2Cl_2$	160	White	51	CH_2Cl_2	2044
$[CpIrP(C_6H_5)_3(CO)C_6H_{13}]^+I^-.\frac{1}{2}CH_2Cl_2$	120	White	47	CH_2Cl_2	2043
$[CpIrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$	180	White	90	CH_2Cl_2	2045
$[CpIrP(C_6H_5)_3(CO)C_3F_7]^+I^-$	185	Yellow	61	CH_2Cl_2	2086
$[CpIrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$	155	White	85	CH_2Cl_2	2063

TABLE XV (continued)

$CpIrP(C_6H_5)_3(CO)\cdot ZnBr_2$	220	Pale-Yellow	85	CH_2Cl_2	2005
				$(CH_3)_2CO$	1928
				Nujol mull	2000
$CpIrP(C_6H_5)_3(CO)\cdot HgCl_2$	260	Pale-Yellow	90	CH_2Cl_2	2024
				$(CH_3)_2CO$	2020
				Nujol mull	2017
$CpIrP(C_6H_5)_3(CO)\cdot TlCl_3$	160	Pale-Yellow	89	CH_2Cl_2	2050
				$(CH_3)_2CO$	2047
				Nujol mull	2062m,2045m

higher basicity of XXXII, although a complex of XXXII with the weaker Lewis acid, $ZnBr_2$, does dissociate in acetone.

^{1}H Nmr Spectra. At least two sets of resonances were observed in each spectrum (Table XVI) and these can be attributed to the phenyl protons of the phosphorus ligand and the cyclopentadienyl protons. The phenyl resonances show typical complex structures and thus for each compound, only the chemical shift of the most intense line is listed in Table XVI.

Spectral data were obtained for most compounds. However, the ionic dihalides and the neutral Lewis acid adducts did not allow measurement since they were too insoluble in the common solvents, deuterochloroform or carbon tetrachloride.

As expected, phosphorus caused the cyclopentadienyl resonances to appear as doublets and the size of this coupling was similar to that in related rhodium compounds (Table XIII).

The unique iridium proton in the compound $[CpIrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$ was confirmed by a broad doublet at high field; the doublet is clearly due to phosphorus coupling, and the wide nature of these peaks is probably caused by coupling to the five cyclopentadienyl protons (see nmr discussion of $CpCORh(H)Si(C_6H_5)_3$, Chapter V). The chemical shift and coupling constant of the single proton were in agreement with other phosphorus-substituted iridium hydrides (192,193,194).

TABLE XVI

^1H NMR Spectral Data [a]

Compound	Solvent	$\tau_{C_6H_5}$	τ_{C_p}	τ_R [b]	J_{P-C_p} [c]	J_{P-R} [c]
$CpIrP(C_6H_5)_3(CO)$	CCl_4	2.68	5.00		0.6	
$CpIrP(C_6H_5)_3Cl_2$	$CDCl_3$	2.51	4.60		1.5	
$CpIrP(C_6H_5)_3Br_2$	$CDCl_3$	2.57	4.62		1.4	
$CpIrP(C_6H_5)_3I_2$	$CDCl_3$	2.57	4.58		1.5	
$[CpIrP(C_6H_5)_3(CO)CH_3]^+Cl^-\cdot\frac{1}{2}CH_2Cl_2$ [d]	$CDCl_3$	2.43	3.95	8.87	1.1	5.1
$[CpIrP(C_6H_5)_3(CO)CH_3]^+Br^-\cdot\frac{1}{2}CH_2Cl_2$ [d]	$CDCl_3$	2.42	3.95	8.85	1.2	5.1
$[CpIrP(C_6H_5)_3(CO)CH_3]^+I^-\cdot\frac{1}{2}CH_2Cl_2$ [d]	$CDCl_3$	2.43	3.98	8.84	1.2	5.0
$[CpIrP(C_6H_5)_3(CO)C_2H_5]^+I^-\cdot\frac{1}{2}CH_2Cl_2$ [d]	$CDCl_3$	2.40	3.98	8.47(4) [e]	1.1	
				7.07(1) [e]		
$[CpIrP(C_6H_5)_3(CO)C_6H_{13}]^+I^-\cdot\frac{1}{2}CH_2Cl_2$ [d]	$CDCl_3$	2.40	4.00	8.87 [e]	1.1	
$[CpIrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$	$CDCl_3$	2.36	4.17	5.84(1) [e]	1.1	
				6.90(1) [e]		
$[CpIrP(C_6H_5)_3(CO)C_3F_7]^+I^-$	$CDCl_3$	2.37	3.73		1.0	
$[CpIrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$ [f]	$(CD_3)_2CO$	2.44		24.42		25

TABLE XVI (continued)

Footnotes to Table XVI

[a] Measured at 60 Mc at 40°.

[b] The symbol R refers to the alkyl protons or single proton directly attached to iridium.

[c] Recorded in cps.

[d] These derivatives exhibited one resonance at τ 4.70 ($\pm$ 0.02), integrating to one proton, attributable to dichloromethane.

[e] Refers to center of unresolved resonances and the number in brackets corresponds to the number of protons by integration.

[f] The spectrum of this compound was recorded at 100 Mc.

For the methyliridium complexes $[CpIrP(C_6H_5)_3(CO)CH_3]^+$-$X^-$, the resonances are independent of X as would be predicted for such ionic compounds. The couplings of phosphorus to the cyclopentadienyl and methyl protons are consistent with those in $[CpRhP(CH_3)_2C_6H_5(CO)CH_3]^+[B(C_6H_5)_4]^-$ (see Figures 20 and 21), confirming the tentative assignments made for the latter compound. The ethyl, hexyl and benzyl derivatives of XXXII give complex resonances for the alkyl group; in particular the α methylene group (and possibly a β methylene group) would be expected to exhibit an AB pattern due to the asymmetry around iridium, and further splitting is likely from coupling to phosphorus and β protons. The resonances of each compound were found to integrate correctly.

EXPERIMENTAL SECTION

The reaction methods employed were as described in previous chapters. The collection of microanalytical (Table XVII) and physical data were also made by procedures already mentioned.

The starting material $[(C_6H_5)_3P]_2Ir(CO)Cl$ [often known as Vaska's compound (195) although first prepared by Angoletta (196)] was prepared by the method of Collman *et al* (152). Wilkinson's compound $[(C_6H_5)_3P]_3RhCl$ was obtained using the original synthesis (160).

Preparation of $CpIrP(C_6H_5)_3(CO)$. A 1M solution of sodium cyclopentadienide in tetrahydrofuran (20 ml) was evaporated to dryness. Benzene (100 ml) and $[(C_6H_5)_3P]_2Ir(CO)Cl$ (3.5 g, 5 mmol) were added and the mixture refluxed for 6 hr. After cooling and filtering through a short column of Florisil the filtrate was concentrated to 5 ml. Addition of hexane (25 ml) and cooling to -15° yielded bright orange crystals of product (1.64 g, 3 mmol, 60%).

Preparation of $CpRhP(C_6H_5)_3(CO)$. Tristriphenylphosphinerhodium chloride (1.0 g, 1.08 mmol) was suspended in benzene (25 ml) and carbon monoxide was bubbled through the mixture for 1 hr. After this time the solid and solution had become pale yellow, indicating the formation of $[(C_6H_5)_3P]_2Rh(CO)Cl$. This product was reacted as was $[(C_6H_5)_3P]_2Ir(CO)Cl$ in benzene solution with excess sodium cyclopentadienide (6 ml of 1M solution in tetrahydrofuran). Using the work-up procedure of

the analogous iridium system, orange crystals of the required product (0.24 g, 0.51 mmol, 48%) were obtained, m.p. 153 - 155° (literature 153° (131)). Analysis for $CpRhP(C_6H_5)_3(CO)$, calculated C, 62.90; H, 4.40: Found C, 63.34; H, 4.22.

Preparation of $[CpIrP(C_6H_5)_3(CO)Cl]^+Cl^-$. The compound $CpIrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) was dissolved in toluene (10 ml), cooled to liquid nitrogen temperature, and chlorine was (0.09g, 1.27 mmol) distilled in. The mixture was allowed to warm to -78°, and excess chlorine was removed under reduced pressure. Addition of pentane (10 ml) and warming to -30° yielded a light yellow microcrystalline powder. This was collected and washed twice with 10-ml portions of pentane keeping the temperature close to -30°. After drying under high vacuum, the yield was 0.34 g, 0.55 mmol, 86%.

Preparation of $[CpIrP(C_6H_5)_3(CO)Br]^+Br^-$. A solution of bromine (0.10 g, 0.63 mmol) in dichloromethane (10 ml) was added to a stirred solution of $CpIrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) in dichloromethane (10 ml). After 10 minutes, hexane (20 ml) was added and the mixture was cooled to 0°. The small yellow crystals of product which formed were collected, washed with pentane (5 ml) and dried (yield 0.42 g, 93%).

A similar procedure using iodine in place of bromine was used to prepare $[CpIrP(C_6H_5)_3(CO)I]^+I^-$ in 85% yield.

Preparation of $CpIrP(C_6H_5)_3Cl_2$. The ionic derivative $[CpIrP(C_6H_5)_3(CO)Cl]^+Cl^-$ (0.20 g, 0.32 mmol) was refluxed in toluene (20 ml) for 3 days. After filtering off some black decomposition product, the filtrate was cooled to -15° to afford yellow crystals of the required product (0.05 g, 0.08 mmol).

Using this procedure, the neutral complexes $CpIrP(C_6H_6)_3Br_2$ and $CpIrP(C_6H_5)_3I_2$ were prepared from the corresponding ionic halides with reaction times of 3 days and 12 hr respectively.

Preparation of $[CpIrP(C_6H_5)_3(CO)CH_3]^+Cl^-.\frac{1}{2}CH_2Cl_2$. Methyl chloride (2 ml) was distilled into a Carius tube in which had been placed a sample of $CpIrP(C_6H_5)_3(CO)$ (0.30 g, 0.55 mmol). After sealing and allowing the mixture to stand at room temperature for 5 days, excess methyl chloride was removed under reduced pressure. The solid residue was taken up in dichloromethane (3 ml) and this solution added slowly to 30 ml of stirred diethyl ether. The resulting white precipitate was collected and recrystallised from dichloromethane/diethyl ether to give silvery white crystals (0.27 g, 0.42 mmol).

Methyl bromide was reacted similarly for a period of 3 days with subsequent recrystallisation from dichloromethane/hexane to give $[CpIrP(C_6H_5)_3(CO)CH_3]^+Br^-.\frac{1}{2}CH_2CH_2$.

Preparation of $[CpIrP(C_6H_5)_3(CO)CH_3]^+I^-.\frac{1}{2}CH_2Cl_2$. A sample of $CpIrP(C_6H_5)_3(CO)$ (0.55 g, 1.0 mmol) was dissolved in

dichloromethane (10 ml) and methyl iodide (1.0 g, 7.0 mmol) added. The mixture was stirred for 15 min and hexane (40 ml) added. A white crystalline precipitate formed which was recrystallised from dichloromethane/hexane (yield, 0.61 g, 89%).

Preparation of $[CpIrP(C_6H_5)_3(CO)C_2H_5]^+I^-.\frac{1}{2}CH_2Cl_2$. Ethyl iodide (2.0 ml, 3.9 g, 25 mmol) was added to a solution of $CpIrP(C_6H_5)_3(CO)$ (0.55 g, 1.0 mmol) in dichloromethane (10 ml). The mixture was allowed to stand for 48 hr and evaporated to dryness. The residue was recrystallised from dichloromethane/benzene to give silvery-white crystals. Subsequent recrystallisation from dichloromethane/hexane afforded the analytically pure compound (0.38 g, 0.51 mmol, 51%).

Benzyl iodide was reacted in similar fashion for a period of 12 hr to yield $[CpIrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$.

Preparation of $[CpIrP(C_6H_5)_3(CO)C_6H_{13}]^+I^-.\frac{1}{2}CH_2Cl_2$. Dichloromethane (5 ml) was used to dissolve $CpIrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) and n-hexyl iodide (1.0 ml, 1.44 g, 6.8 mmol) added. After one week, solvent and excess halide were removed under reduced pressure. The remaining solid was recrystallised three times from dichloromethane/diethyl ether to afford the required product (0.24 g, 0.30 mmol).

Preparation of $[CpIrP(C_6H_5)_3(CO)C_3F_7]^+I^-$. The compound $CpIrP(C_6H_5)_3(CO)$ (0.30 g, 0.55 mmol) was dissolved in dichloromethane (5 ml), the solution cooled to -70° and

perfluoropropyl iodide (3.0 g, 10.1 mmol) added. The mixture was allowed to attain room temperature over a period of 2 hr and hexane (10 ml) added. The solid produced was collected and recrystallised from dichloromethane/hexane to yield yellow crystals (0.28 g, 0.33 mmol, 61%).

Preparation of $[CpIrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$. A sample of $CpIrP(C_6H_5)_3(CO)$ (0.35 g, 0.64 mmol) was dissolved in dichloromethane (10 ml) and, after cooling to -70°, hydrogen bromide was passed through the solution until the yellow color had completely disappeared. Addition of pentane (30 ml) and warming to room temperature produced small white crystals which were collected, washed with two 10 ml portions of pentane and dried. Part of this product (0.17 g) was dissolved in methanol (10 ml) and a solution of sodium tetraphenylboron (0.17 g, 0.50 mmol) in methanol (10 ml) immediately added. The solution was stirred for 10 min and the white precipitate which had formed was collected. After washing with two 5-ml portions of methanol, 5-ml of pentane and drying, the yield of product was 0.20 g, 0.23 mmol.

Preparation of $CpIrP(C_6H_5)_3(CO)\cdot HgCl_2$. Mercuric chloride (0.174 g, 0.639 mmol) was dissolved in a 1:2 methylethylketone:benzene mixture (10 ml) and a solution of $CpIrP(C_6H_5)_3$-(CO) (0.350 g, 0.639 mmol) in the same solvent (5 ml) was added quickly with vigorous stirring. The resultant pale yellow precipitate was collected, washed with acetone (10 ml) and dried (yield, 0.473 g, 0.578 mmol).

Reactions with zinc bromide and thallic chloride were

carried out using the procedure outlined above; however, in the former case, the final washing was done with the methylethylketone:benzene mixture, not acetone. Thus the adducts $\underline{CpIrP(C_6H_5)_3(CO)\cdot ZnBr_2}$ and $\underline{CpIrP(C_6H_5)_3(CO)\cdot TlCl_3}$ were produced.

TABLE XVII

Analytical Data

Compound	Calculated %				Found %			
	C	H	X^a	P	C	H	X^a	P
$CpIrP(C_6H_5)_3(CO)$	52.64	3.68			53.09	3.94		
$[CpIrP(C_6H_5)_3(CO)Cl]^+Cl^-$	46.60	3.26			46.90	3.31		
$CpIrP(C_6H_5)_3Cl_2$	46.78	3.41			46.65	3.45		
$[CpIrP(C_6H_5)_3(CO)Br]^+Br^-$	40.75	2.85	22.59	4.38	40.70	2.80	21.56	4.14
$CpIrP(C_6H_5)_3Br_2$	40.66	2.97			41.33	2.98		
$[CpIrP(C_6H_5)_3(CO)I]^+I^-$	35.97	2.52	31.67	3.86	35.90	2.94	31.42	3.66
$CpIrP(C_6H_5)_3I_2$	35.72	2.61	32.81	4.00	35.76	2.66	33.04	3.88
$[CpIrP(C_6H_5)_3(CO)CH_3]^+Cl^-\cdot\frac{1}{2}CH_2Cl_2$	47.81	3.78			48.02	3.63		
$[CpIrP(C_6H_5)_3(CO)CH_3]^+Br^-\cdot\frac{1}{2}CH_2Cl_2{}^b$	44.71	3.53	11.67	4.52	44.89	3.71	11.57	4.39
$[CpIrP(C_6H_5)_3(CO)CH_3]^+I^-\cdot\frac{1}{2}CH_2Cl_2$	41.84	3.30			41.59	3.60		
$[CpIrP(C_6H_5)_3(CO)C_2H_5]^+I^-\cdot\frac{1}{2}CH_2Cl_2{}^c$	42.66	3.51	17.01	4.15	42.65	3.14	17.45	4.14
$[CpIrP(C_6H_5)_3(CO)C_6H_{13}]^+I^-\cdot\frac{1}{2}CH_2Cl_2$	45.66	4.27			44.88	4.44		
$[CpIrP(C_6H_5)_3(CO)CH_2C_6H_5]^+I^-$	48.63	3.55	16.57	4.05	48.28	3.67	17.01	4.05
$[CpIrP(C_6H_5)_3(CO)C_3F_7]^+I^-$	38.44	2.39			38.28	2.51		
$[CpIrP(C_6H_5)_3(CO)H]^+[B(C_6H_5)_4]^-$	66.43	4.76		3.57	66.74	4.85		3.03
$CpIrP(C_6H_5)_3(CO)\cdot ZnBr_2$	37.30	2.61			37.55	2.39		

TABLE XVII (continued)

$CpIrP(C_6H_5)_3(CO)\cdot HgCl_2$	35.19	2.46	3.78	8.66	35.25	2.67	3.78	8.56
$CpIrP(C_6H_5)_3(CO)\cdot TlCl_3$	33.58	2.35			33.92	2.66		

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[a] The symbol X refers to halogen and if two different halogens are present in the same compound X represents the halogen of larger atomic number.

[b] Calculated Cl = 5.18, Found Cl = 5.10.

[c] Calculated Cl = 4.75, Found Cl = 4.91.

CHAPTER VIII

A STUDY OF CYCLOPENTADIENYL(TRIPHENYLPHOSPHINE)-ETHYLENERHODIUM AND RELATED COMPOUNDS

It has been seen in the previous two chapters that the compounds CpMLY (M = Rh or Ir, L = phosphine and Y = CO) can undergo oxidation: (i) with retention of Y to give an ionic compound [VII.3]; (ii) with insertion of Y into a newly formed bond [VI.3]; (iii) with complete elimination of Y [VI.1]. Ligands other than CO might behave similarly but in order that the three modes of reaction can remain, Y must be capable of acting as an insertion reagent (197,198). The other possibilities for Y are then virtually limited to isocyanides (199), sulfur dioxide (200) or olefins (201,202,203,204).

The compounds chosen for study were $CpRhL(C_2H_4)$, since reactions of ethylene derivatives have implications for a number of olefin analogues and such compounds might have applications in the field of catalysis (205).

RESULTS AND DISCUSSION

By analogy with the preparation of $CpRh(CO)P(CH_3)_2C_6H_5$ from $CpRh(CO)_2$, (Chapter VI), it might be considered that a ligand could displace ethylene from $CpRh(C_2H_4)_2$ to afford a compound of the type $CpRhL(C_2H_4)$. This reaction only takes place if L has some Lewis acid character (as mentioned in Chapter IV), presumably because there is no mechanism for attack if L is a base

such as triphenylphosphine. In a 16-electron rather than 18-electron system there is a means of attack, for an 18-electron complex could form as an intermediate. Thus displacement of ethylene by triphenylphosphine was attempted in acetylacetonatobisethylenerhodium. Substitution of one ethylene ligand was achieved in similar fashion to the substitution of carbon monoxide in acetylacetonatodicarbonylrhodium (206). Subsequent reaction of $(CH_3COCHCOCH_3)$-$Rh(C_2H_4)P(C_6H_5)_3$ with sodium cyclopentadienide gave the required compound, $CpRhP(C_6H_5)_3(C_2H_4)$ (XXXVII) in moderate yield.

Attempts to prepare the analogous triphenylarsine complex by this method were without success; this seems to be attributable to incomplete replacement of a single ethylene ligand from $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$ at temperatures where general decomposition was minimal.

Another possible method of obtaining the compound $CpRhP(C_6H_5)_3(C_2H_4)$ is by using the route employed for $CpRhP(C_6H_5)_3(CO)$ (see Chapter VII), that is, to displace triphenylphosphine from Wilkinson's compound, $[(C_6H_5)_3P]_3$-$RhCl$, giving $[(C_6H_5)_3P]_2Rh(C_2H_4)Cl$ (XXXVIII) and reacting this product with sodium cyclopentadienide. The ethylene in XXXVIII is very labile (160) and appears to be lost so easily that it is not retained in the latter reaction. In the arsine complex analogous to XXXVIII (207) the ethylene is not as labile and so reaction [VIII.1] affords a reasonable yield of $CpRhAs(C_6H_5)_3(C_2H_4)$ (XXXIX).

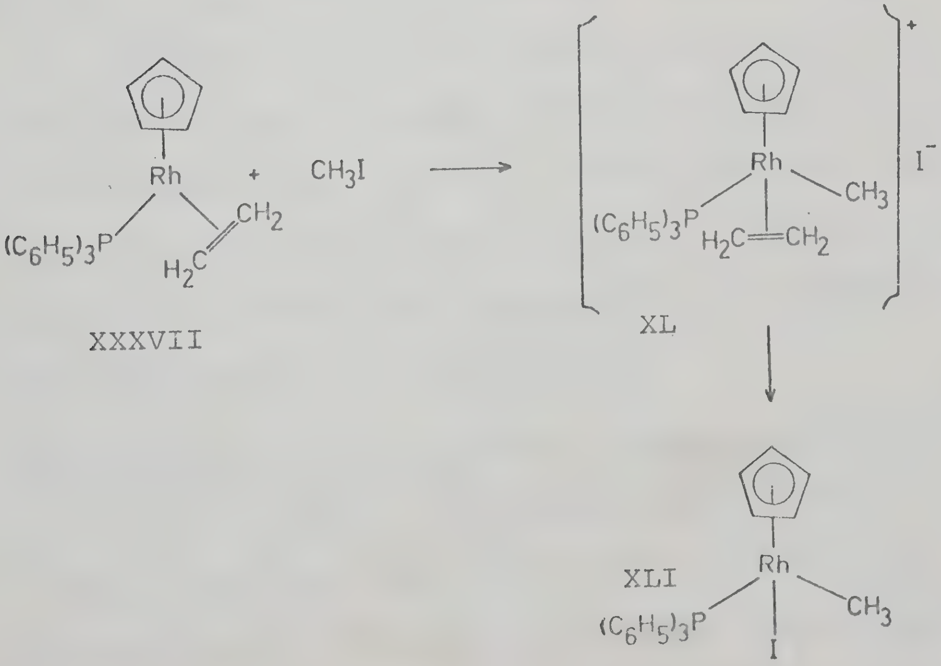
$$[(C_6H_5)_3As]_2Rh(C_2H_4)Cl + C_5H_5Na \longrightarrow \underset{\text{XXXIX}}{CpRhAs(C_6H_5)_3(C_2H_4)} + NaCl + As(C_6H_5)_3 \qquad [VIII.1]$$

Reactions of halogens with XXXVII can be anticipated to give compounds of the type $CpRhP(C_6H_5)_3X_2$ (137) and this was confirmed by the reaction with iodine [VIII.2].

$$CpRhP(C_6H_5)_3(C_2H_4) + I_2 \longrightarrow CpRhP(C_6H_5)_3I_2 + C_2H_4 \qquad [VIII.2]$$

This reaction presumably takes place *via* an ionic intermediate (see [VI.1]), but no evidence for this was actually observed.

In the reaction of methyl iodide with XXXVII, a pale colored solid was formed initially, presumably $[CpRhP(C_6H_5)_3(C_2H_4)CH_3]^+I^-$ (XL) [VIII.3]. A light color appears from



XXXVII

XL

XLI

[VIII.3]

previous work (Chapters VI and VII) to be typical of ionic compounds of this type. The intermediate (XL) rapidly decomposes with elimination of ethylene to form $CpRhP(C_6H_5)_3$-CH_3I (XLI). Although the ionic derivative (XLI) could not be obtained in a pure state it was possible to isolate the arsine analogue by reaction of XXXIX with methyl iodide. This is consistent with a comparison of the compounds $[(C_6H_5)_3P]_2Rh(C_2H_4)Cl$ and $[(C_6H_5)_3As]_2Rh(C_2H_4)Cl$, where ethylene is lost more easily from the former than from the latter.

For both phosphine and arsine reactions [VIII.3] there was evidence for small yields of diiodides, $CpRhLI_2$. Since an attempt was made to ensure that the methyl iodide was free of iodine initially, either iodine was produced by a mechanism which may or may not involve the transition metal or the compound $CpRhLCH_3I$ undergoes a further reaction. More work is necessary to clarify this feature.

Reactions similar to [VII.3] occurred on treatment of XXXVII with methyl bromide or benzyl bromide but no ionic intermediates were observed. Stannic bromide yields the compound $CpBrRhP(C_6H_5)_3SnBr_3$ although it did not seem possible to prepare this compound by the reaction of triphenylphosphine with $CpCOBrRhSnBr_3$.

^{1}H NMR Spectra. The parameters obtained from measurement of the ^1H nmr spectra are listed in Table XVIII and some of the spectra are shown in Figures 22, 23 and 24. The cyclopentadienyl and phenyl resonances were similar to

TABLE XVIII

^1H NMR Spectral Data

Compound	Solvent	$\tau_{C_6H_5}$	τ_{Cp}	τ_R [b]	J_{Cp-P} [c]	J_{Cp-Rh} [c]	J_{R-P} [b,c]	J_{R-Rh} [b,c]
$CpRhP(C_6H_5)_3(C_2H_4)$	$(CD_3)_2CO$	2.59	4.91	7.48, 9.08[d]	1.1	0.7	...	...
$CpRhAs(C_6H_5)_3(C_2H_4)$	$(CD_3)_2CO$	2.57	4.87	7.58, 8.93[d]	...	0.8	...	...
$CpRhP(C_6H_5)_3I_2$	$CDCl_3$	2.55	4.55	...	2.1	0[e]	...	...
$CpRhP(C_6H_5)_3CH_3I$	$CDCl_3$	2.59	4.87	8.61	1.8	0.5	6.2	2.5
$CpRhAs(C_6H_5)_3CH_3I$	$CDCl_3$	2.55	4.80	8.49	...	0.5	...	2.6
$CpRhP(C_6H_5)_3CH_3Br$	$CDCl_3$	2.57	4.92	8.57	1.7	0.5	6.4	2.4
$CpRhP(C_6H_5)_3(CH_2C_6H_5)Br$	$CDCl_3$	2.57	5.30	6.52[f]	1.7	0.5	3.8(A) 12.0(B)	3.8(A) 2.3(B)
$CpRhP(C_6H_5)_3SnBr_3Br$	$CDCl_3$	2.52	4.57	...	1.7	0[e]	...	...

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[a] Measured at 60 Mc at 40°

[b] R refers to methyl or methylene protons

[c] Coupling constants are reported in cps.

[d] The τ values reported refer to the centres of each part of a complex doublet.

[e] A value of $J_{Cp-Rh} = 0$ indicates that no rhodium coupling was observed and therefore $J_{Cp-Rh} \leq 0.4$ cps.

[f] The AB part of an ABMX pattern was observed; separation between A (lower field) and B (higher field) resonances is 0.38 ppm, $J_{AB} = 8.1$ cps.

those observed for related compounds in Chapters VI and VII.

The ^{1}H nmr spectrum of CpRh$(C_2H_4)_2$ has been discussed in detail by Cramer (104), and in particular the energy associated with rotation of the ethylene ligands was determined. At the temperature of 40° employed for the work reported here, the ethylene resonances for compounds (XXXVII and XXXIX) are little changed from those observed for the parent bisethylene compound (104). Deuteroacetone was used as solvent for the ethylene derivatives reported here since they seem to be unstable in chlorinated solvents.

The spectra of the compounds CpRhP$(C_6H_5)_3CH_3I$ (Figure 22) and CpRhAs$(C_6H_5)_3CH_3I$ (Figure 23) were useful in confirming the assignment of rhodium and phosphorus coupling to both methyl and cyclopentadienyl protons. It can be seen that phosphorus has the larger coupling to both of these sets of protons.

The asymmetry of the compound CpRhP$(C_6H_5)_3(CH_2C_6H_5)$Br was confirmed by a chemical shift separation between the resonances of the two methylene protons (208). The difference between this chemical shift and coupling constants was determined by measurement of the spectra at 100 Mc as well as 60 Mc (Figure 24). The expected AB pattern was further split by coupling to rhodium and phosphorus. Very different couplings were observed from phosphorus to the individual methylene protons, as has been found for the related compound CpCOFeP$(C_6H_5)_3CH_2$Si-

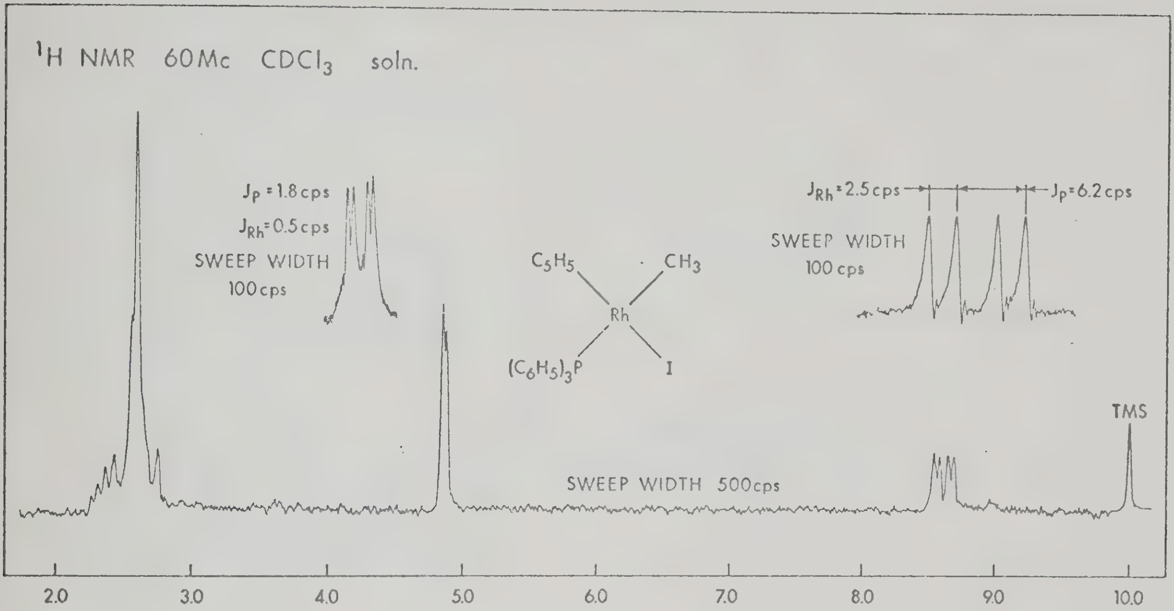

FIGURE 22: The ^{1}H NMR Spectrum of $CpRhP(C_6H_5)_3CH_3I$.

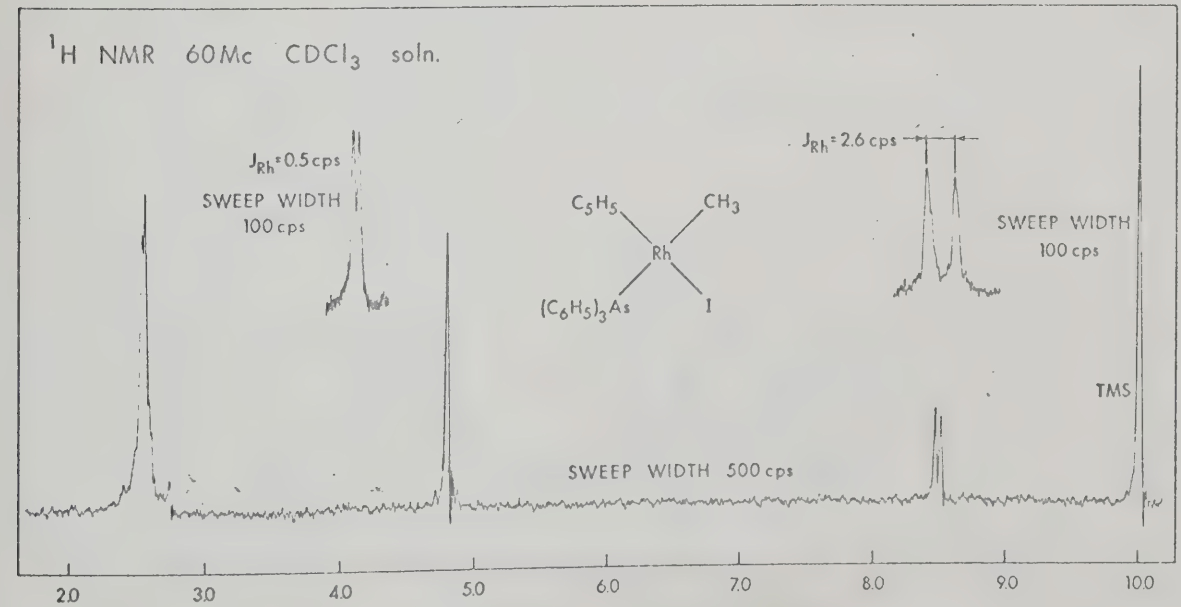

FIGURE 23: The ^{1}H NMR Spectrum of $CpRhAs(C_6H_5)_3CH_3I$.

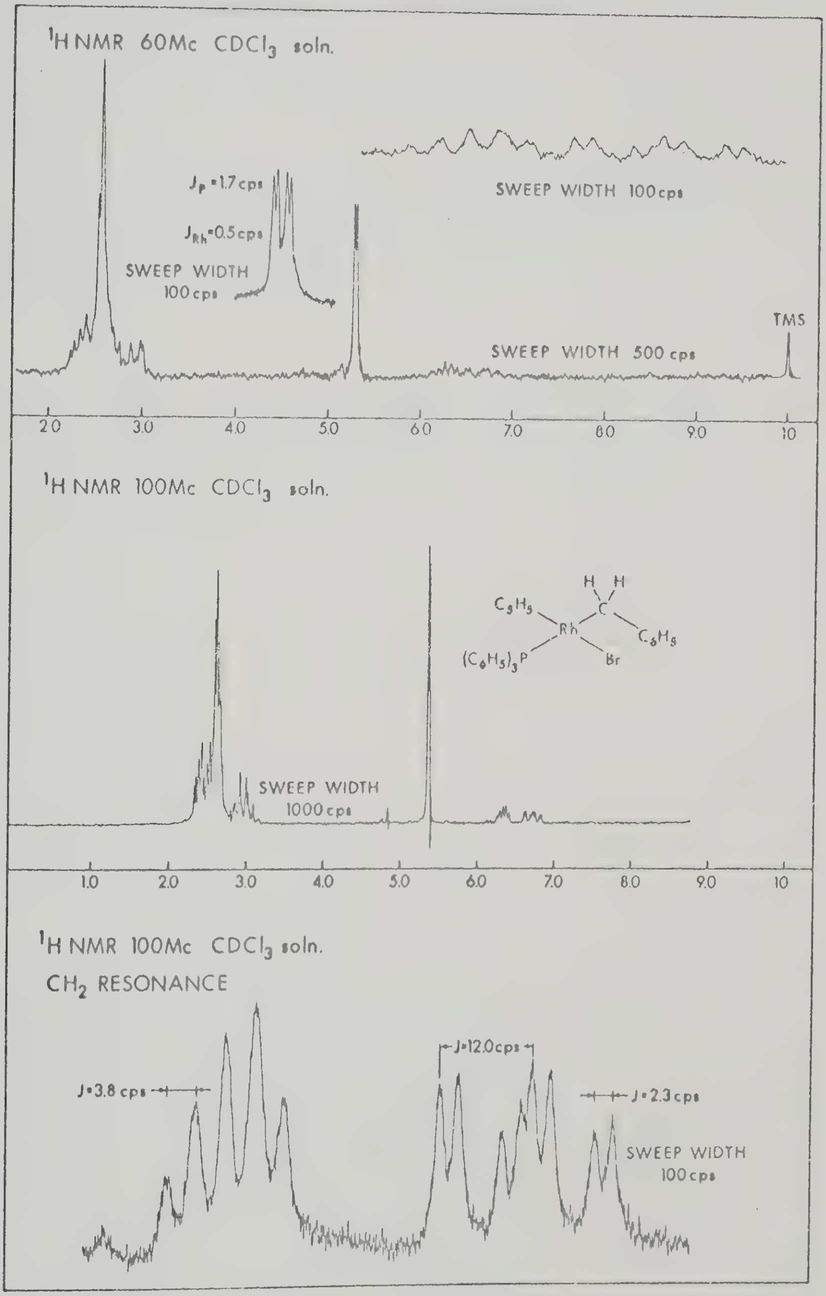

FIGURE 24: The ^{1}H NMR Spectrum of $CpRhP(C_6H_5)_3(CH_2C_6H_5)Br$.

$(CH_3)_3$ (J_{A-P} = 2 cps, J_{B-P} = 13 cps) (181). It is interesting to note that in contrast to the *gem*-protons mentioned here, *gem*-methyl groups in, for example, $CpRhP(CH_3)_2C_6H_5$-$(COCH_3)Br$, appear to couple equally to both rhodium and phosphorus.

All resonances were found to integrate correctly for the formulae proposed.

EXPERIMENTAL SECTION

The reaction methods employed were as described in previous chapters. Microanalytical (Table XIX) and physical data (Tables XVIII and XX) were collected in ways already mentioned.

The starting materials $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$ (104) and $[(C_6H_5)_3As]_2Rh(C_2H_4)Cl$ (207) were prepared by literature methods. Other reagents were obtained and purified as described previously.

Preparation of $(CH_3COCHCOCH_3)Rh(C_2H_4)P(C_6H_5)_4$. A solution of freshly crystallised triphenylphosphine (1.25 g, 4.8 mmol) in dichloromethane (5 ml) was added slowly to $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$ (1.2 g, 4.8 mmol) also dissolved in dichloromethane (5 ml). Evolution of gas took place, and after stirring the mixture for 1 hr and concentrating to 5 ml, hexane (20 ml) was added. Orange crystals of product (1.26 g, 2.56 mmol, 53%) were obtained on cooling to 0°.

Preparation of $CpRhP(C_6H_5)_3(C_2H_4)$. A solution of 1M sodium cyclopentadienide (10 ml, 10 mmol) in tetrahydrofuran was evaporated to dryness and to this was added $(CH_3COCHCOCH_3)$-$Rh(C_2H_4)P(C_6H_5)_3$ (1.26 g, 2.56 mmol) dissolved in benzene (30 ml). The mixture was stirred for 24 hr and filtered through a short column of Florisil. The resulting orange solution was concentrated to 5 ml and hexane (20 ml) added. Cooling to -15° afforded orange crystals of the required compound (0.61 g, 1.33 mmol, 52%).

Preparation of $CpRhAs(C_6H_5)_3(C_2H_4)$. Benzene (30 ml) was used to dissolve $[(C_6H_5)_3As]_2Rh(C_2H_4)Cl$ (3.88 g, 4.98 mmol) and the solution added to dry solid sodium cyclopentadienide formed by evaporation of a 1M solution in tetrahydrofuran (25 ml). The mixture was stirred for two days, filtered through a short column of Florisil, and concentrated to 5 ml. Addition of hexane (20 ml) and cooling to -15° produced orange-red crystals of the required compound (0.96 g, 1.91 mmol, 38%).

Preparation of $CpRhP(C_6H_5)_3I_2$. The compound $CpRhP(C_6H_5)_3$-(C_2H_4) (0.23 g, 0.50 mmol) was dissolved in dichloromethane (10 ml) and iodine (0.13 g, 0.50 mmol) added. After stirring for 30 min, hexane (10 ml) was added and the mixture cooled to 0°. Fine black needles of product (0.30 g, 0.44 mmol, 88%) were isolated.

Preparation of $CpRhP(C_6H_5)_3CH_3I$. Methyl iodide (3.0 ml, 6.8 g, 48 mmol) was added to $CpRhP(C_6H_5)_3(C_2H_4)$ (0.40 g, 0.87 mmol). Complete solution took place and then a very pale solid rapidly precipitated out. This precipitate dissolved in dichloromethane to give a very dark solution which was chromatographed on a column of Florisil using dichloromethane as eluant. First collected was an orange-red band and then a very deep red band. The solutions containing the two bands were individually concentrated to a small volume and hexane added to give crystalline products on cooling. The first product was found to be pure

$CpRhP(C_6H_5)_3CH_3I$ (0.34 g, 0.59 mmol, 68%). The second (0.05 g) was found spectroscopically to be predominantly the diiodide with some of the methyliodo-derivative.

Reaction of $CpRhAs(C_6H_5)_3C_2H_4$ with CH_3I. The compound $CpRhAs(C_6H_5)_3(C_2H_4)$ (0.29 g, 0.58 mmol) was dissolved in methyl iodide (0.50 ml, 1.14 g, 8.0 mmol) and after stirring for about 1 min a light precipitate formed. Diethyl ether (20 ml) was added and the solid collected. This was recrystallised from methanol/diethyl ether to afford pale yellow needles of $[CpRhAs(C_6H_5)_3(C_2H_4)CH_3]^+I^-$ (0.12 g, 0.19 mmol, 32%). The remaining methyl iodide/diethyl ether and methanol/diethyl ether solutions were evaporated to dryness and the combined solid residues dissolved in dichloromethane (10 ml). After stirring for 12 hr the solution was subjected to chromatography on a column of Florisil with dichloromethane as solvent. A red-orange band was collected first and was followed by a red-brown band. The solutions containing the two bands were separately evaporated down to 5 ml and pentane (20 ml) added. The first product, which formed as orange-brown crystals, was shown to be $CpRhAs(C_6H_5)_3CH_3I$ (0.09 g, 0.15 mmol, 25%). The second solution afforded black crystals of $CpRhAs(C_6H_5)_3I_2$ (0.01 g, 0.01 mmol, 2%).

Preparation of $CpRhP(C_6H_5)_3CH_3Br$. The compound $CpRhP(C_6H_5)_3(C_2H_4)$ (0.40 g, 0.87 mmol) was placed in a Carius tube and methyl bromide (3.5 g, 37 mmol) was added by distillation.

After sealing, the mixture was allowed to stand at room temperature for 3 days and excess methyl bromide then removed under reduced pressure. The resulting solid was chromatographed on a Florisil column using dichloromethane as solvent. The required compound appeared as an orange band and was first to be eluted. A small red band remained on the column but this could not be removed by dichloromethane. The solution of $CpRhP(C_6H_5)_3CH_3Br$ was concentrated to 3 ml and hexane (10 ml) added to afford bright orange crystals (0.28 g, 0.53 mmol, 61%).

Preparation of $CpRhP(C_6H_5)_3(CH_2C_6H_5)Br$. Benzyl bromide (1.0 ml, 1.44 g, 8.4 mmol) was added to a solution of $CpRhP(C_6H_5)_3(C_2H_4)$ in dichloromethane (5 ml). After stirring for 12 hr the mixture was subjected to chromatography on a Florisil column using dichloromethane as eluant. The first dark red band was collected, concentrated to 5 ml and hexane was added. A small yield of a compound presumed to be $CpRhP(C_6H_5)_3Br_2$ was first obtained but addition of more hexane gave the require compound (0.24 g, 0.40 mmol, 40%).

Preparation of $CpRhP(C_6H_5)_3SnBr_3Br$. Stannic bromide (0.22 g, 0.50 mmol) was added to a stirred solution of $CpRhP(C_6H_5)_3$-(C_2H_4) (0.23 g, 0.50 mmol) in dichloromethane (15 ml). After 1 hr, hexane (30 ml) was added to give red crystals, which were recrystallised twice from dichloromethane/hexane. Thus a sample of pure product (0.21 g, 0.24 mmol, 48%) was isolated.

TABLE XIX

Analytical Data

Compound	Calculated %				Found %			
	C	H	X	P or As	C	H	X	P or As
$(CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4)$	60.99	5.32		6.29	61.15	5.28		6.59
$CpRhP(C_6H_5)_3(C_2H_4)$	65.51	5.28		6.76	65.99	5.03		6.98
$CpRhAs(C_6H_5)_3(C_2H_4)$	59.78	4.83		14.92	59.76	4.77		14.79
$CpRhP(C_6H_5)_3I_2$	40.38	2.95	37.10	4.53	40.51	2.91	37.33	4.58
$CpRhAs(C_6H_5)_3I_2$	37.94	2.76			37.94	2.76		
$CpRhP(C_6H_5)_3CH_3I$	50.37	4.05	22.18	5.41	50.20	4.13	22.37	5.28
$[CpRhAs(C_6H_5)_3CH_3(C_2H_4)]^+I^-$	48.47	4.22			47.92	4.02		
$CpRhAs(C_6H_5)_3CH_3I$	46.78	3.76			46.63	3.67		
$CpRhP(C_6H_5)_3CH_3Br$	54.88	4.41			54.78	4.30		
$CpRhP(C_6H_5)_3(CH_2C_6H_5)Br$	59.92	4.53			59.44	4.50		
$CpRhP(C_6H_5)_3SnBr_3\ Br$	31.80	2.32			31.74	1.95		

TABLE XX

Physical Properties

Compounds	m.p. °C[a]	Color	% Yield
$(CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4)$	135	yellow	53
$CpRhP(C_6H_5)_3(C_2H_4)$	150	orange-red	52
$CpRhAs(C_6H_5)_3(C_2H_4)$	143	orange-red	38
$CpRhP(C_6H_5)_3I_2$	260	black	88
$CpRhAs(C_6H_5)_3I_2$	275	black	2[b]
$CpRhP(C_6H_5)_3CH_3I$	174	orange-brown	68
$[CpRhAs(C_6H_5)_3(C_2H_4)CH_3]^+I^-$	60	pale-yellow	32[b]
$CpRhAs(C_6H_5)_3CH_3I$	190	orange-brown	25[b]
$CpRhP(C_6H_5)_3CH_3Br$	193	orange-red	61
$CpRhP(C_6H_5)_3(CH_2C_6H_5)Br$	145	red	40
$CpRhP(C_6H_5)_3SnBr_3\ Br$	120	red	48

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[a] All compounds decompose over a 5 - 10° range

[b] These compounds were produced in the same reaction, therefore overall percentage yield is 59%.

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B29968